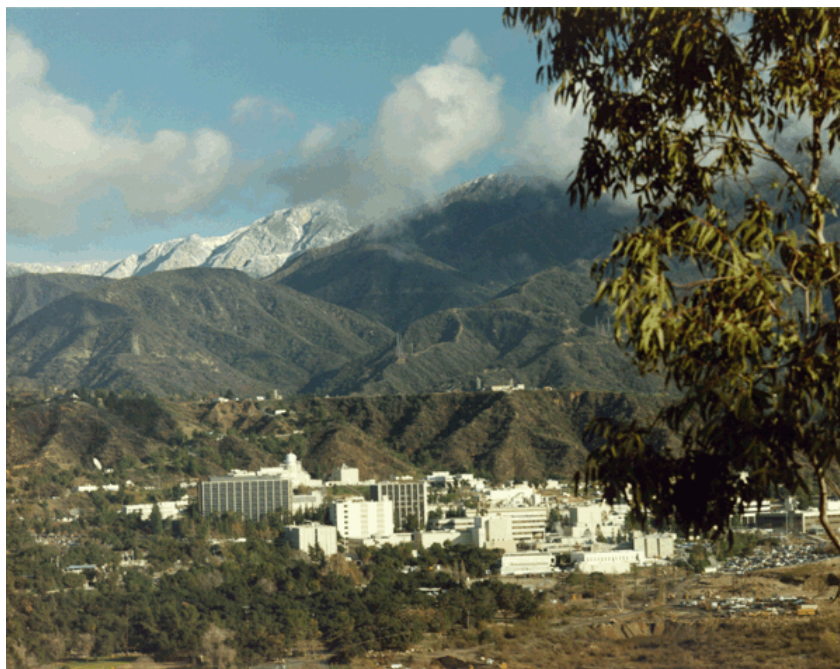


FINAL

**PERCHLORATE (ClO_4^-) TREATMENT TECHNOLOGIES LITERATURE REVIEW
OPERABLE UNIT 1 EXPANDED TREATABILITY STUDY**

**NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
JET PROPULSION LABORATORY
PASADENA, CALIFORNIA**

EPA ID# CA9800013030



PREPARED FOR:



**National Aeronautics and Space Administration
Management Office, Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, California 91101**

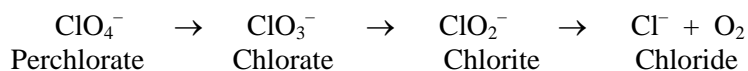
June 2006

The use of conventional water treatment technologies has proven to be largely ineffective for perchlorate (ClO_4^-) removal because of its low reactivity, low volatility, and high solubility (Urbansky, 1999). Therefore, scientists, regulators, responsible parties, and others in the environmental community have participated in a substantial effort to develop and test more effective methods for the treatment of perchlorate-impacted groundwater. The primary challenge has been to develop technologies that can meet the low ClO_4^- effluent levels required to protect human health, while still cost-effectively treating the large volumes of water handled during remediation and/or drinking water supply projects.

A literature review was completed in order to provide an updated assessment of the development status of various biological, physical, chemical, and thermal treatment technologies used for the removal of ClO_4^- from groundwater. This review consisted primarily of an analysis of published scientific articles, review articles, trade journal articles, recent patents, conference proceedings, and other selected reports available through the United States Environmental Protection Agency (U.S. EPA) Region 9 Superfund Records Center. The primary objective of the review was to highlight the lessons learned from several recent field-scale projects. These results will help to focus the efforts of the planned expanded treatability study at the National Aeronautics and Space Administration (NASA) Jet Propulsion Laboratory (JPL) on those ClO_4^- treatment technologies that have the following characteristics: (1) a proven track record of effectiveness in achieving ClO_4^- removal and/or destruction, (2) a history of successful field-scale implementation at JPL or other sites, and (3) favorable project economics.

The Ground Water Remediation Technologies Analysis Center (GWRTAC) recently completed a *Technology Status Report for Perchlorate Treatment Technologies* (2001) and identified 65 laboratory, pilot-scale, and full-scale projects for the remediation of ClO_4^- in soil and groundwater. The report determined that biological treatment methods were the most frequently implemented and/or studied at 69% of case studies, physical methods at 22%, chemical methods at 6%, and 3% unspecified methods. The primary treatment technologies covered in this review are biological, physical, chemical, and thermal methods. The results of several key case studies identified during this literature review are presented. This literature review focuses primarily on projects that have been implemented at the field-scale, but laboratory results are discussed when the studies were completed in conjunction with a field-scale project and/or when no field-scale projects were identified.

It has been widely demonstrated in the literature that ClO_4^- is readily degraded by microbes and that these microbes are present in a variety of environments including pristine and hydrocarbon-contaminated soils, aquatic sediments, and industrial and agricultural waste sludges (Gingras and Batista, 2002). Although the reduction of ClO_4^- is a thermodynamically favorable reaction, the reaction is impeded by a high activation energy, which makes ClO_4^- very chemically stable under normal groundwater and surface water conditions (Urbansky, 1999). However, perchlorate-reducing microbes produce an enzyme that allows them to lower the activation energy for ClO_4^- reduction and to use ClO_4^- as an alternate electron acceptor for metabolism in place of oxygen or nitrate. In order to carry out ClO_4^- reduction, the microbes first need an organic or inorganic electron donor source (e.g., ethanol or H_2 gas) for growth and then utilize the ClO_4^- molecule as a terminal electron acceptor. The enzyme-catalyzed reduction from ClO_4^- to chlorate to chlorite is completed as follows to produce the nontoxic by-products of chloride and oxygen (Logan, 1998).



It is clear that both ex situ and in situ biological treatment methods have great potential for the remediation of perchlorate-contaminated groundwater. In fact, more than 69% of the case studies in the GWRTAC study relied upon the biological degradation of ClO_4^- as part of their treatment methodology. Forty-five percent (45%) of the case studies used ex situ biological treatment, 18% used in situ biological treatment, and 6% relied upon an unspecified general biological treatment technique (GWRTAC, 2001). A discussion of key case studies for both ex situ and in situ biological treatment methods are provided below.

Ex Situ Biological Treatment

Ex situ biological treatment involves extracting groundwater from the subsurface and pumping it through a reactor containing a large population of microbes. A steady supply of electron donor is pumped into the reactor to support microbial growth and the subsequent reduction of ClO_4^- . Ex situ biological treatment is one of the most frequently studied and/or implemented ClO_4^- treatment technologies, representing 45% of the case studies in the GWRTAC technology status report (GWRTAC, 2001). The appeal of this treatment method is likely tied both to the ability of microbes to break ClO_4^- down into the nontoxic by-products of chloride and oxygen and to the potential for substantial economic savings over physical and/or chemical treatment methods. One study showed that ex situ biological treatment capital costs were 25% less expensive than a patented ion exchange process, whereas annual operation and maintenance costs were more than 57% less expensive (Harding ESE, 2001). Ex situ biological treatment can be used to treat perchlorate-contaminated groundwater directly or to treat brine wastes generated from separation processes such as reverse osmosis and ion exchange (Gingras and Batista, 2002). The use of biological treatment systems for drinking water purposes is not widespread in the United States and physical and chemical processes are typically viewed as the more conventional approach (Logan, 1998). However, full-scale ex situ biological treatment systems have been carefully evaluated in terms of their process effectiveness, reliability, and control and found to consistently produce treated water to non-detectable levels of perchlorate. The State of California Department of Health Services (DHS) recently accepted the use of biological treatment to remove or reduce perchlorate from source water that might be used as a potable water supply (DHS, 2002).

Several parameters must be considered in the design, construction, and operation of an ex situ biological treatment system including the selection of an appropriate electron donor and the bioreactor configuration.

Based on this review and others, acetate has been used extensively as an electron donor in both laboratory and field studies (Logan, 1998). However, as shown in Table F-1, several other amendments have been tested including ethanol, methanol, H₂ gas, yeast extract, and other food processing wastes. The selection of an amendment is based on several considerations including cost, availability, presence of other chemicals, and favorable kinetics or performance with respect to ClO₄⁻ reduction. Significant cost savings can be generated through the selection of inexpensive amendments that are waste by-products from the food processing industry or other sources (ESTCP, 2000).

Several types of bioreactor configurations are available, including continuously stirred tank reactors (CSTRs), packed bed reactors (PBRs), and fluidized-bed reactors (FBRs). According to GWRTAC, CSTRs represent 31% of all ex situ biological case studies, PBRs represent 22%, and FBRs are the most frequently utilized bioreactor configuration at 37% of all ex situ biological case studies. The remaining 10% of case studies involved unspecified types of bioreactors. In addition, the commercialization of FBRs appears to be significantly ahead of CSTRs and PBRs, as several of the reported case studies are large-scale pilot and/or full-scale FBR systems rather than laboratory and/or small-scale pilot tests. CSTR applications have generally been limited to the treatment of high-strength industrial wastewaters and not perchlorate-contaminated groundwater where effective treatment of low concentrations (e.g., ~100 µg/L) requires different engineering considerations. In addition, only a few small-scale PBR pilot projects have been implemented and reported in the literature to date with mixed results. In general, PBRs have been reported to have lower ClO₄⁻ loading rates and more problems with biofouling and process reliability compared with FBRs (Harding Lawson Associates, 1999).

Below, each type of reactor configuration is discussed, along with the key results from several case studies. Also included below is a discussion of more experimental electron donor amendments (e.g., hydrogen) and reactor types (e.g., hollow fiber membrane) that have been reported in the literature.

Continuously Stirred Tank Reactors (CSTRs)

CSTRs involve the development of an active biomass, which is kept in suspension in a liquid-filled tank by mechanical mixing. CSTRs are well suited to the treatment of low flowrates and high concentration industrial wastes. CSTRs are most likely unsuitable for groundwater treatment applications where high flowrates greater than 1,000 gallons per minute (gpm) and low concentrations must be effectively treated (Hatzinger et al., 2002). Residence times for these types of bioreactors are typically on the order of 2 to 4 hours (U.S. EPA, 1993), although one study reported a residence time as high as 24 hours, as opposed to minutes for attached growth bioreactors like PBRs and FBRs (see Table F-1). Because CSTRs are better suited for the treatment of very highly concentrated wastes, they have been implemented as part of a treatment train with ion exchange units. This approach involves using the CSTR to treat the effluent brine created from the regeneration of the ion exchange resin. Applied Research Associates (ARA) has several patents pending and has implemented this treatment train approach at the Thiokol Corporation in Utah as discussed below. This vendor reports that the combination of ion exchange with biological treatment of the brine can be cost-effective at \$100 to \$200 per acre-foot (ARA, 2003).

CSTRs at Tyndall Air Force Base in Florida, Thiokol Corporation in Utah, and Hodgdon Powder Company in Kansas

A study conducted by the Air Force Research Laboratory (AFRL) reported the development of a 450-gpm CSTR system to remove ammonium perchlorate in process wastewater and secondary waste brine streams

from the production, remanufacturing, testing, and demilitarization of Minuteman II propulsion systems. The pilot-scale system was first tested at Tyndall Air Force Base in Florida and the full-scale system was then installed and operated at Thiokol Corporation in Utah. The primary components of the CSTR system included two bioreactors that could be operated in parallel or series, a clarifier to aid in the retention of biomass, and various feed and waste storage tanks (ESTCP, 2000).

The objectives of the demonstration were to identify a low-cost amendment alternative, to demonstrate that the process was effective and reliable, and to show that a broad range of wastewater compositions could be treated. Several electron donor amendments were tested including brewer's yeast, cheese whey, marshmallow waste, fruit juice wastes, sugars, starches, and acetate. Food waste or carbohydrate by-product was found to be the most effective and economical amendment (\$0.16/lb vs. \$1.75/lb of ClO_4^- for brewer's yeast). The influent to the CSTR consisted of ClO_4^- brine (~2,800 to 41,000 mg/L) that was diluted to provide a monthly average feed concentration between 300 and 4,600 mg/L. The brine was diluted to provide relatively constant influent conditions because higher ClO_4^- levels >6,000 mg/L were found to inhibit microbial activity.

Perchlorate was consistently removed to levels ranging from 4 to 400 $\mu\text{g/L}$ in the effluent. (The wastewater discharge permit at the facility specified a maximum effluent limit of 10 mg/L for ClO_4^-). Effective treatment was achieved despite the additional challenge of treating wastewater with a high salt content (>2.3% Na^+ , K^+ , Cl^-) and other impurities (NO_2^- , NO_3^- , and SO_4^{2-}). Chemical oxygen demand (COD) and total suspended solids (TSS) in the effluent were both relatively high at 5,000 mg/L due to both excess nutrients and suspended cell biomass. It was noted that the elevated COD and TSS might necessitate additional treatment in order to discharge the treated water to a publicly owned treatment works (POTW). The CSTR process was shown to operate reliably over a five-year demonstration period and operation is still ongoing. In 1999 alone, more than 15,400 lb of ClO_4^- was destroyed at the Thiokol Corporation plant. In general, nutrient, brine, and dilution flowrates were maintained close to target levels during both the pilot-scale and full-scale operations. However, excursions were noted when ClO_4^- levels exceeded 6,000 mg/L and nutrient limiting conditions were experienced.

High temperatures were also found to adversely impact treatment effectiveness and resulted from heat generation caused by an inadequately sized pump, which was later removed from operation. In addition, some plugging or biofouling was experienced in nutrient feed lines and control valves. Over the duration of the study, several optimization steps were taken to select the most cost-effective amendment, to reduce the residence time, to reduce the operating temperature, and to directly feed undiluted nutrients and supplements into the CSTR (ESTCP, 2000).

ARA has also recently completed the installation of a full-scale wastewater treatment system for Hodgdon Powder Company in Herington, Kansas. The CSTR treats wastewater with perchlorate and nitrate concentrations greater than 3,000 mg/L (ARA, 2003).

Table F-1. Selected Ex Situ Biological Treatment Case Study Results

Author	Scale	Reactor Type	Media Type	Reactor Size	HRT	Total Flowrate	Amendments	Initial [Final] ClO ₄ ⁻ Levels	Initial [Final] Nitrate Levels
ESTCP, 2000	P	CSTR	NA	1,600 gal and 720 gal	18 to 24 hrs	NA	Brewers Yeast Extract	4,000 to 10,000 mg/L [<0.5 mg/L]	346 to 4,622 mg/L
ESTCP, 2000	F	CSTR	NA	1,600 gal and 720 gal	10 to 20 hrs	450 gpm	Carbohydrate By-product	300 to 4,600 mg/L [4 to 400 µg/L]	5,000 mg/L
Hatzinger et al., 2002	P	FBR	GAC	15 ft tall by 20 dia	NA	30 gpm	Ethanol	770 µg/L [<4 µg/L]	33.2 mg/L [<0.4 mg/L]
Hatzinger et al., 2000	F	FBR	GAC	4 Units 22 ft tall by 14 ft dia	12 min	4,000 gpm	Ethanol	4,000 to 6,000 µg/L [<4 µg/L]	6.5 mg/L [<0.4 mg/L]
Guarini, 2002	F	FBR	GAC	1 Unit 21 ft tall and 5 ft dia	NA	50 gpm	Acetic Acid	15,000 µg/L [<4 µg/L]	1.9 mg/L
Togna et al., 2001	L	FBR	GAC	4 L	NA	NA	Acetic Acid and Ethanol	25,000 µg/L [<5 µg/L]	1.9 mg/L
Evans et al., 2002	P	PBR	Plastic and Sand Modules	7 ft tall by 2 ft ² x-section	NA	1 to 2 gpm	Acetic Acid	75 µg/L [<4 µg/L to 4.8 µg/L]	4.3 mg-N/L [NA]
Perlmutter et al., 2000	P	PBR	Bio-Rings (3/4 to 2")	2,600 gal 5-ft dia and 18 ft tall	60 min	43 gpm	Acetate	23,000 µg/L [<20 µg/L]	NA
Perlmutter et al., 2000	L	PBR	Sand	2.2 gallons	30 to 80 min	20 to 80 mL/min	Acetate	1 to 5 mg/L [<20 µg/L]	NA
Perlmutter et al., 2000	L	PBR	Plastic Beads	2.2 gallons	20 to 130 min	25 to 160 mL/min	Acetate	1 to 5 mg/L [<20 µg/L]	NA
Perlmutter et al., 2000	L	PBR	Bio-Rings (5/8")	2.2 gallons	45 to 300 min	25 to 160 mL/min	Acetate	1 to 5 mg/L [<20 µg/L]	NA
Wallace et al., 1998 ^a	L	PBR	Diatomaceous Earth Pellets	1.2 m tall by 7.6 cm in dia	0.5 to 1 hr	NA	Brewers Yeast Extract	1,500 mg/L [<100 mg/L]	NA
Logan and Kim (1998) ^a	L	PBR	Sand	14.2 cm tall	NA	NA	Acetate	20 mg/L [<4 µg/L]	NA
Giblin et al., 2000	L	PBR	Diatomaceous Earth Pellets	120 mL 18 cm tall by 3.5 cm dia	2 hrs	1 mL/min	Hydrogen and Bicarbonate	740 µg/L [<4 µg/L]	NA
Giblin et al., 2000	L	PBR	Diatomaceous Earth Pellets	NA	NA	1 mL/min	Acetate	738 µg/L [<04 µg/L]	NA
Van Ginkel et al., 1998 ^a	L	Gas-Lift Reactor	Pumice	NA	6 hrs	NA	Hydrogen Gas	>95% chlorate removal	NA
Rittmann et al., 2002	P	Hollow Fiber	Composite Membrane	13 m ² surface area	NA	NA	Hydrogen Gas	60 µg/L [3 µg/L]	24 [<0.5 mg/L]

HRT= hydraulic residence time

PBR = packed bed reactor

FBR = fluidized bed reactor

CSTR= continuously stirred tank reactor

NA = not applicable.

(a) Source: Logan, 1998.

(b) Source: Perlmutter et al., 2000.

CSTR Study at Jet Propulsion Laboratory in California

A laboratory-scale study was conducted for JPL to evaluate the use of a CSTR for the treatment of reverse osmosis (RO) rejectates. A simulated RO rejectate was first developed based on the composition of groundwater and the results of previous RO testing at the JPL site. The study demonstrated the rapid development of a perchlorate-reducing culture in a lab-scale CSTR. The microbes were supplied with the same inexpensive food by-product used above in the Thiokol Corporation demonstration project. Although several excursions were experienced during testing, overall it was demonstrated that ClO_4^- could be successfully removed from the surrogate RO brine (at ~ 10 mg/L) to non-detect levels (< 20 $\mu\text{g/L}$). The excursions or temporary treatment failures during CSTR operation were due primarily to loss of nutrient and/or water flow, pH control problems, and programmable logic control (PLC) or sensor malfunctions. It was estimated in this study that the CSTR process would be able to reduce ClO_4^- within a residence time of 1 to 4 hours (ARA, 2000).

Conclusions

It is not likely that the CSTR configuration alone would be appropriate for ex situ groundwater treatment at JPL. The primary reason is because of the high residence time predicted in the lab-scale study. Another limitation is the potential for high concentrations of organic matter in the system effluent due to both high nutrient loading requirements and suspended cell biomass (Logan, 1998). The treatment train approach with an ion exchange system coupled with a CSTR for brine treatment may be a viable option depending on site-specific economics. The overall advantages and limitations associated with this technology are listed below:

Advantages

- CSTRs can be used to effectively treat very highly contaminated ClO_4^- wastes.
- CSTRs can be used to reduce ClO_4^- in high salinity ($> 2\%$) wastewaters.
- The CSTR process is well understood and the system is easily maintained.
- Biological treatment methods are typically less expensive in terms of operation and maintenance costs compared to physical/chemical processes.
- Biological treatment methods typically generate less hazardous waste than physical/chemical processes.

Limitations

- Concentrations above 6,000 to 10,000 mg/L appear to inhibit ClO_4^- reduction by microbes.
- Some other chemicals in wastewater (e.g., isopropyl alcohol) may inhibit ClO_4^- reduction by microbes.
- High organic matter present in CSTR effluent may require additional treatment.
- High residence times limit the ability to treat high flowrates.

- Process is reliable, but upsets can occur from suboptimal electron donor dosing, pH changes, temperature changes, or other conditions.
- Loss of biological activity could interrupt operation for several days.

Packed Bed Reactors

PBRs utilize an attached growth process to stimulate and sustain ClO_4^- degradation. Instead of growing suspended in a liquid as with a CSTR, the biomass in a PBR attaches and grows on a filter media placed inside the reactor. As Table F-1 shows, the filter media can consist of a variety of materials including sand, GAC, plastic rings, and other materials. The filter media is sized and selected to provide a large surface area for contact between the microbes and perchlorate-impacted groundwater and to facilitate flow to obtain the necessary hydraulic residence time. The packed bed also reduces the need for downstream filtration or clarification as used with suspended growth reactors such as the CSTR. However, because of the gradual accumulation of suspended solids and cell biomass in the PBR filter media, the reactor will require periodic backwashing to prevent excessive headlosses (U.S. EPA, 1993). Packed beds are reported to have a tendency for channeling and clogging during long-term operation (Hatzinger et al., 2002; Evans et al., 2002). Backwashing frequencies are typically every 1 to 5 days depending on operational conditions. Backwashing consists of flushing with an air/water wash to slough off excess biomass (U.S. EPA, 1993). After backwashing, there may be some loss of accumulated biomass and additional time may be required to reestablish adequate ClO_4^- reducing performance. Several laboratory scale studies of PBRs have been completed using a variety of filter media and a variety of amendments (see Table F-1). However, to date, only a few field-scale systems appear to have been implemented and reported in the literature as discussed below.

PBR Study at Crafton-Redlands Site in California

A pilot-scale PBR was constructed at the Crafton-Redlands site in Redlands, California where groundwater contains both ClO_4^- and chlorinated volatile organic compounds (VOCs). The chlorinated VOCs were removed using a GAC unit and nitrate and ClO_4^- removal was tested in an up-flow PBR with side-by-side plastic and sand filter media modules. The pilot test was run over a period of 138 days. The up-flow PBR had a cross-sectional area of 2 ft² and the reactor height was 7 ft. Acetic acid was selected as the electron donor for this pilot-scale test. The flowrates tested in the PBR ranged from 1 to 2 gpm. Influent ClO_4^- levels were at approximately 75 µg/L, the groundwater was saturated with dissolved oxygen at 8.9 mg/L, and nitrate levels were at 4.3 mg/L. For the plastic packing material, effluent ClO_4^- levels of <4 µg/L were not consistently achieved during the testing period. Backpressures of up to 200 inches of H₂O were observed during the initial two months of testing and this reportedly led to channeling and inadequate residence time in the reactor. Weekly backwashing was then carried out to maintain backpressures at levels less than 100 in H₂O for the duration of the test. Once a backwashing strategy was implemented, a flowrate of 1 gpm resulted in an average effluent ClO_4^- level of less than 4 µg/L, but a flowrate of 2 gpm resulted in an average ClO_4^- effluent level of 4.8 µg/L. It was reported that the sand media was more severely impacted by backpressure and channeling problems and ClO_4^- removal results were not reported for the PBR sand module. Although the study successfully demonstrated that PBRs can obtain ClO_4^- effluent levels less than 4 µg/L, the study concluded that the primary challenge with running a PBR appears to be establishing an effective backwashing strategy to prevent channeling and clogging (Evans, 2002).

PBR Study at McGregor Naval Weapons Industrial Reserve Plant in Texas

ClO_4^- reduction in a PBR was tested at both the bench scale and pilot scale at the Naval Weapons Industrial Reserve Plant (NWIRP) in McGregor, TX. The studies were carried out to demonstrate the feasibility of ClO_4^- reduction in a PBR and to provide data for scale-up of a pump and treat system that would collect groundwater from a cutoff trench at the site boundary. Several parameters were of interest including the optimal water flowrate and media type and the impact of ClO_4^- concentrations and groundwater geochemistry on the bioreactor's performance. The groundwater at NWIRP McGregor contained ClO_4^- at levels ranging from $<4 \mu\text{g/L}$ to $91,000 \mu\text{g/L}$.

For the bench-scale tests, five different media were used including 5/8-inch Bio-Rings, 1-inch Bio-Rings, cylindrical plastic pellets, U.S. Silica Sand, and gravel. In addition, three carbon sources were evaluated including citric acid, fructose, and potassium acetate. The bench-scale reactors were first inoculated with activated sludge from the City of McGregor POTW and KJ-1, a cultured perchlorate-reducing microorganism. After the biomass had developed in the reactors, perchlorate-impacted groundwater was passed through the reactors at flowrates between 0.6 and 10 mL/min during Phase I testing and 25 and 160 mL/min during Phase II testing. During the bench-scale testing, initial ClO_4^- concentrations ranged from 30,000 to 100,000 $\mu\text{g/L}$. The 5/8-inch Bio-Rings were found to be the most effective filter media because they were the least expensive, exhibited more ClO_4^- removal at higher surface loading rates, and were less conducive to clogging than the other media that were tested. Phase II bench-scale testing demonstrated that a PBR of 5/8-inch Bio-Rings, with an acetate amendment, could consistently reduce ClO_4^- to less than 20 $\mu\text{g/L}$ (the detection limit due to high nutrient levels). Reliable reduction was achieved at flowrates up to 160 mL/min or a surface loading rate of $4.2 \times 10^{-4} \text{ gpm/ft}^2$. Hydraulic residence times ranged from 45 to 300 minutes. By comparison, reliable reduction with sand was achieved only at flowrates up to 80 mL/min, which corresponds to a much lower surface loading rate of $1.0 \times 10^{-5} \text{ gpm/ft}^2$.

Based on the above results, a 43 gpm pilot-scale PBR was constructed on site and consisted of a 5-ft-diameter, 18-ft-tall bioreactor filled with 2-inch and 3/4-inch Bio-Pac media. In order to limit the amount of wastewater generated during the test, the PBR was operated as a closed-loop system or with continuous recirculation of a finite amount of water. The pilot-scale test was run over a 28-day period. After inoculation, it took approximately one week for the biomass to develop in the bioreactor. ClO_4^- influent levels ranged from approximately 7,000 to 23,000 $\mu\text{g/L}$. The PBR was able to consistently reduce ClO_4^- levels down to less than 20 $\mu\text{g/L}$. The detection limit was elevated above the 4 $\mu\text{g/L}$ laboratory method detection limit because of the high total dissolved solids (TDS) in the groundwater which ranged from 2,850 mg/L at the start to $>5,000 \text{ mg/L}$ at the end of the test. The increasingly high TDS levels were due primarily to the test configuration, which called for continuous recirculation of the treated water. The pilot-scale test demonstrated that ClO_4^- could be effectively reduced at a rate of 12 lb/day or a surface loading rate of $1.5 \times 10^{-3} \text{ gpm/ft}^2$. The retention time was measured at 60 minutes. No major excursions were noted over the 28 days of operation and no observations of clogging or channeling were discussed in the literature. Despite the successful treatment demonstration, the pilot-scale PBR system was not taken to full-scale at NWIRP McGregor. Instead, an innovative in situ permeable reactive barrier was installed to prevent off-site migration of ClO_4^- as opposed to the previously planned groundwater pump and treat system (Perlmutter et al., 2000).

PBR Lab Studies at Jet Propulsion Laboratory in California

The lab-scale study for JPL consisted of PBR column studies to demonstrate the feasibility of ClO_4^- reduction in both groundwater and simulated RO rejectates. The PlexiglasTM column used in the study was 13.5 cm in diameter and 21.4 cm in height with a total volume of 3,062 mL. Celite was used as the

filter media. The test column was inoculated with a cultured perchlorate-reducing microbe called *perclace* identified previously by Herman and Frankenberger (1999). Acetate was used as the carbon source during these tests. Each column test lasted approximately four weeks. Although some excursions occurred due to periodic failures of the acetate pump and a temporary lack of electron donor supply, treatment before and after these brief upset conditions was effective for both groundwater and the primary RO rejectate. It was demonstrated that the PBR system was able to reduce ClO_4^- in JPL groundwater from 800 $\mu\text{g/L}$ to non-detect ($<4 \mu\text{g/L}$) at a residence time as low as 0.3 hour. In addition, the PBR reduced ClO_4^- in the primary RO rejectate from 5 mg/L to non-detect ($<4 \mu\text{g/L}$) with a residence time of less than 0.8 hour. Secondary RO rejectate could not be treated to non-detect levels, which indicated that *perclace* was inhibited at the higher ClO_4^- influent levels. However, 90% removal was achieved (from 10 mg/L to 0.2 mg/L) during a 2.1 hr residence time. Other results from the laboratory tests indicated that nitrate was effectively removed in all three waste streams, there was no need for nitrogen addition, and sulfate reduction did not occur in any of the column tests (Losi et al., 2001).

PBR Field Studies at Jet Propulsion Laboratory in California

Several field-scale PBR configurations were tested at NASA JPL during a phased pilot program as discussed below:

Phase I was conducted in the spring of 2001. During this phase, three 6 gpm PBR reactor configurations were field tested at the site. The pilot system consisted of three PBRs packed with Celite® R-633, which is a diatomaceous earth product with a sand-like consistency and relatively high surface area. The three test PBRs were set up in parallel. Each reactor was associated with a different combination of biological inoculum and carbon source. These combinations included *perclace* with acetate, food waste/compost with ethanol, and cultures isolated from JPL with acetate. The reactors were first operated in recycle mode for several weeks, while discharge approval was negotiated. Upon initiation of forward flow mode, the pilot-scale reactors were shown to successfully reduced ClO_4^- concentrations in groundwater from 0.42 mg/L to less than 4 $\mu\text{g/L}$. However, after less than one week of operation the reactors experienced channeling and plugging and perchlorate breakthrough was observed.

The Phase II testing occurred in the summer and fall of 2002. The Phase II pilot system consisted of two bioreactors in series packed with Hydroxyl-PAC® high-density polyethylene media and two bioreactors in series packed with polyethylene sponge scrubbers impregnated with Celite® R-635 pellets. The reactors were filled only about two-thirds full to allow for movement and suspension of the media. This reactor configuration was referred to as a dynamic suspended bed reactor (DSBR). The DSBR was expected to provide improved flow characteristics by using different media with less surface area and greater pore volume than used in Phase I testing. The extra space in the vessels allowed for bed expansion unlike the PBRs tested previously. The substrate of sodium acetate was added at a concentration of 300 mg/L. Nutrients were added at 1.0 and 0.9 mg/L as hydrogen phosphate ($\text{HPO}_4\text{-P}$) and ammonium nitrogen ($\text{NH}_4\text{-N}$), respectively. Phase II tests showed that both packing materials showed promise as media for ClO_4^- reduction, but the reactor with Hydroxyl-PAC® media had slightly better overall performance. The reactor inoculated with *perclace* was found to perform better than the reactor with the JPL isolates for ClO_4^- removal. NO_3^- was reduced to non-detectable levels by both reactors throughout the test. However, the perchlorate removal rates were only at 70% to 80% for influent concentrations from 1.5 up to 10.5 mg/L.

Conclusions

Based on the results of several laboratory and full-scale studies, it is clear that PBRs have a high potential for channeling and clogging and that this adversely impacts full-scale process effectiveness, reliability,

and control. PBRs are also reported to handle lower ClO_4^- loading rates than FBRs (Harding Lawson Associates, 1999). In addition, because of limited field-scale experience with these systems and lack of a dedicated commercial vendor, it is unlikely that a PBR configuration would be appropriate for ex situ groundwater treatment at JPL at this time. The overall advantages and limitations associated with this technology are listed below:

Advantages

- PBRs have much lower residence time requirements than CSTRs due to the advantages of attached growth mechanisms and increased biofilm surface area.
- PBR pumping requirements and costs are less than FBRs because lower total flowrates and recycle rates can be used without the need for fluidized media.
- Biological treatment methods are typically less expensive in terms of operation and maintenance costs compared to physical/chemical processes.
- Biological treatment methods typically generate less hazardous waste than physical/chemical processes.

Limitations

- PBRs appear to be prone to channeling and clogging, and frequent backwashing may be needed.
- Frequent backwashing may impair the ability of the biomass to degrade ClO_4^- .
- Process is reliable, but upsets can occur from suboptimal electron donor dosing, pH changes, temperature changes, or other conditions.
- Loss of biological activity could interrupt operation for several days.

Fluidized Bed Reactor

FBRs are similar to PBRs except that the influent flowrate must be high enough to produce a fluidized bed of media. Fluidization means that the media particles are suspended and not in contact with other particles. Fluidization increases the specific surface area available for microbial growth and therefore increases the efficiency of ClO_4^- reduction per unit volume of the reactor. In an FBR, the specific surface area available for microbial growth is 244 to 305 m^2/m^3 of reactor volume compared to approximately 91 m^2/m^3 in a downflow PBR configuration. This advantage can be used to size smaller bioreactors and/or to reduce hydraulic residence times while still obtaining effective ClO_4^- reduction (U.S. EPA, 1993). A more detailed discussion of the configuration and operation of FBR systems will be provided in the three case studies provided below.

FBR Case Study at Aerojet Facility in California

Since 1997, the Aerojet General Corporation has tested and operated both pilot-scale and full-scale FBRs for ClO_4^- removal as part of the groundwater remediation efforts at its facility in Rancho Cordova, California. The constituents of concern in groundwater at the Aerojet site also include chlorinated solvents and other VOCs. An extensive treatability testing program was conducted on the FBR system at Aerojet to demonstrate to the State of California DHS that potable water can be consistently produced by

the selected treatment train. The treatment train consisted of biological treatment, air stripping, filtration, ultraviolet oxidation, granular media filtration, GAC, and chlorine disinfection (Clark et al., 2001). The treated groundwater is then discharged directly to surface water. In April of 2002, the DHS reviewed the results of the Aerojet treatability testing program and accepted the use of biological treatment to remove or reduce perchlorate from source water that might be used as a potable water supply (DHS, 2002). The results of the Aerojet site pilot-scale and full-scale treatability tests with FBRs are discussed below.

Several laboratory pilot-scale experiments were conducted to optimize the removal of ClO_4^- from groundwater using the FBR process through filter media selection, electron donor selection, and other testing parameters. The filter media tested included GAC with a particle size range from 0.9 to 1.4 mm and sand with a particle size range of 0.3 to 0.6 mm. The electron donors tested included ethanol, methanol, and an ethanol/methanol mixture. The laboratory study was conducted over a four-month period. Each laboratory FBR consisted of a 5-cm-diameter glass column, which was approximately 90 cm in length. Other equipment included the recycle/fluidization pump, feed and effluent pumps, various storage tanks, dissolved oxygen sensors, and an automatic pH control device. The FBRs were operated at room temperature (i.e., 20 to 25°C) and were maintained near a neutral pH of 7.0 to 7.5. A total influent pumping rate of approximately 700 mL/min was needed to maintain fluidization of the media in each reactor. Influent ClO_4^- concentrations ranged from 13 to 28 mg/L during testing. Nitrate levels were at approximately 1.5 mg/L. Dissolved oxygen levels ranged from 1 mg/L to 8 mg/L and were varied during the test to determine the potential impact of pretreatment with air stripping on bioreactor performance. The columns were inoculated with biological solids from a municipal wastewater anaerobic digester in order to develop a perchlorate-reducing biomass. After approximately 34 days of operation, biomass buildup was significant enough to result in more than 0.7 kg/m³/day of ClO_4^- removal in both the GAC and the sand-based FBRs with ethanol as the electron donor. The sand-based FBR with methanol as the only electron donor did not show effective ClO_4^- removal. The conclusions of the pilot test were that a GAC based FBR could achieve a higher level of ClO_4^- reduction than a sand-based FBR. Granular activated carbon- and sand-based FBRs with only methanol as the electron donor were not effective. However, a high level of ClO_4^- reduction could be achieved in both types of reactors with an ethanol/methanol mixture (Sutton and Greene, 1999).

After the laboratory studies discussed above, further testing was completed during a Phase I treatability test using a 30-gpm FBR pilot plant system installed at the site. The objectives of the Phase I testing were as follows: (1) to evaluate lower ClO_4^- influent levels, (2) to evaluate higher nitrate levels, (3) to demonstrate that ClO_4^- effluent levels of <4 µg/L were achievable, (4) to identify a different source of microorganisms, and (5) to evaluate the potability of the treated water. The Phase I pilot-scale test was able to demonstrate the consistent reduction of ClO_4^- from levels between 50 and 100 µg/L in the influent to less than the detection limit of 4 µg/L in the effluent. The system was also able to reduce nitrate levels from 5 to 6 mg/L in the influent to below the detection limit of 0.1 mg/L in the effluent. The pilot plant was inoculated with perchlorate-reducing microbes obtained from food processing industry sludge. No fecal coliform or other human pathogens were identified in the treatment system effluent. The treated water was also analyzed for regulated drinking water parameters and it was determined that additional treatment would be needed to meet disinfection and filtration requirements (Harding Lawson Associates, 1999).

Based on parameters from the laboratory and field pilot-scale studies, a full-scale FBR system was installed at the Aerojet site and has been operating since approximately 1998. Currently, extracted and treated groundwater is being discharged to surface water, but DHS approval has been received for potable water use (DHS, 2002). A Phase II treatability study was performed for more than eight months using this full-scale FBR system in order to further test the reliability of the biological treatment process and to test the entire drinking water treatment train as described previously. The primary objectives of the Phase II testing were as follows: (1) to confirm destruction and removal efficiencies of each unit, (2) to establish

optimal operating parameters for each unit, (3) to collect data to support potable water use, and (4) to collect data for full-scale drinking water treatment plant construction and operation.

The existing pump and treat system at the Aerojet site includes four FBR units, but only one was used during Phase II treatability testing. Each individual unit is rated for up to 1,800 gpm of flow and is 14 ft in diameter and 22 ft tall. GAC was selected as the filter media and ethanol as the electron donor. Fluidization of the reactor media is achieved by passing the influent up through the bioreactor. A fluid distribution system or network of nozzles ensures a uniform upflow velocity across the bottom of the bed. The flowrate must be high enough to achieve at least a 25% to 30% expansion of the bed. At the Aerojet site, a total flowrate of 1,800 gpm in each reactor is needed to achieve fluidization of the media and to obtain a target bed expansion of 33% or a total bed height of 12 ft. At this total flowrate, the hydraulic residence time for each reactor is 14 minutes. The total flow through the FBR consists of both the recycle flow of treated water and the forward flow of untreated groundwater. After startup of the Aerojet system, the forward flow was increased from 240 gpm to approximately 1,400 gpm for the last four months of the Phase II treatability study.

In general, as biomass continues to grow on the FBR media, the particle surface area will increase and the media particles will become less dense. The lowest density particles with the highest attached biomass will then move up to the top of the FBR causing further bed expansion. For this reason, a biomass control system is used at the top of each reactor to remove the excess biomass and to maintain the target bed height. Two different biomass control systems were used on the Aerojet FBR unit during Phase II testing, but some problems were experienced obtaining adequate separation of filter media and sheared biomass. The first biomass control system used consisted primarily of an eductor-type, bed-height limiter that sheared biomass from the GAC and then discharged the clean carbon and sheared biomass back into the reactor. The clean carbon sinks to the bottom of the reactor and the sheared biomass is carried out of the bioreactor in the effluent. A second control device was installed within the bed itself to minimize the overgrowth of filamentous bacteria. Proper biomass control is important as overloading of the biomass into the effluent was shown to cause treatment problems downstream with operation of the multimedia filter (Harding ESE, 2001).

Despite some issues with optimal biomass control, the FBR unit was demonstrated to operate with acceptable stability in removing ClO_4^- from site groundwater. ClO_4^- influent levels ranged from 2 to 7 mg/L. Dissolved oxygen influent levels ranged from 4 to 6.5 mg/L and nitrate influent levels were relatively constant at 1.6 mg/L. After a three-week acclimation period for biomass growth, ClO_4^- was consistently removed to non-detect at $<4 \mu\text{g/L}$ for the duration of the Phase II testing. Dissolved oxygen levels in the effluent ranged from 0.01 to 0.25 mg/L, but were usually less than 0.1 mg/L. Nitrate was consistently removed to non-detect at $11 \mu\text{g/L}$. The only excursions that occurred were caused by forced ethanol-limiting conditions that were brought about during system tests to determine the optimal ethanol dosage for full-scale operation. All four bioreactors at the Aerojet site have continued to operate without excursions or treatment failures as part of the existing pump and treat system at Operable Unit 3. Recommendations for future improvements to the system included adjustments to the biomass control system and the development of a more effective means of on-line monitoring and process control to automate ethanol dosing to the bioreactor (Clark et al., 2001).

FBR Case Study at Longhorn Army Ammunition Plant in Texas

A 50-gpm FBR system was installed at the Longhorn Army Ammunition Plant (LHAAP) in Texas to remove ClO_4^- from groundwater extracted by a pre-existing pump and treat system. The pump and treat system had been originally designed to treat only VOCs and metals. First, a laboratory treatability study was carried out to provide key parameters for full-scale FBR design and to confirm the effectiveness of biological treatment with site groundwater. Acetic acid and ethanol were both tested for their ability to

promote the reduction of ClO_4^- in groundwater from the site. The groundwater used in the study contained approximately 14.7 mg/L of ClO_4^- , 1.9 mg/L of nitrate, and 3.8 mg/L of dissolved oxygen. Granular activated carbon was used as the filter media in the lab-scale FBR and the test reactor was inoculated with biomass and carbon from another perchlorate-reducing laboratory FBR. ClO_4^- removal was observed in the test bioreactor within a few days of inoculation. The project objective was to treat the groundwater to meet the LHAAP wastewater discharge permit limit of 350 $\mu\text{g/L}$ for ClO_4^- . However, during the majority of the laboratory testing, the ClO_4^- effluent levels were below the detection limit of $<5 \mu\text{g/L}$. Both acetic acid and ethanol were found to promote ClO_4^- reduction in LHAAP groundwater. Based on the success of the laboratory study, a full-scale, 50 gpm FBR system filled with granular activated carbon was installed at the site. The FBR system consisted primarily of the reactor vessel (5 ft in diameter and 21 ft tall), fluidization and influent pumps, flow distribution system, chemical feed system, two biomass separation systems to control bed height from the top, and a third in-bed media cleaning system. Acetic acid was selected as the electron donor (Togna et al., 2001). After more than 250 days of full-scale operation, the ClO_4^- effluent concentrations have been consistently below the detection limit of $<4 \mu\text{g/L}$ (Guarini, 2002).

FBR Case Study at Jet Propulsion Laboratory in California

An FBR field pilot test was conducted over a 100-day period at JPL in order to evaluate system performance under site-specific conditions and to provide data to size and cost a full-scale system. The 30-gpm FBR system consisted primarily of a reactor vessel (20 ft in diameter and 15 ft tall), which was filled with granular activated carbon as the filter media. Other components included the fluidization system, biomass control device, and various tanks, pumps, and controls for the addition of electron donor and nutrients, and a system for pH control. In addition, a granular activated carbon system was used to remove VOCs prior to the FBR influent. A post-aeration tank was also supplied to aerate the effluent of the FBR to degrade any excess ethanol prior to discharge. A 9% solution of ethanol was used as the electron donor, along with small amounts of nitrogen and phosphorous as nutrients to promote microbial growth.

The pilot-scale reactor was first inoculated with granular activated carbon from the Aerojet site. After the inoculation, site groundwater was run through the system in a flow forward mode for 27 days and a recycle mode for 22 days. During the recycling period, ethanol and nutrients were added to sustain biological growth and oxygen was periodically added to supply the microbes with an alternate electron acceptor prior to the initiation of the FBR pilot test. After approval to discharge the treated effluent was received, the test was returned to flow forward operation and a 52-day pilot test was initiated. During the test, the maximum flowrate achieved from the groundwater extraction pilot well was 5.2 gpm. This was combined with recycle flow to maintain a total flow of 30 gpm for fluidization of the filter media.

After only three days of operation in this mode, ClO_4^- levels in the influent were reduced from 770 $\mu\text{g/L}$ to $<4 \mu\text{g/L}$ in the effluent and nitrate levels were reduced from 7.5 mg/L in the influent to $<0.1 \text{ mg/L}$ in the effluent. Over the duration of the test, the average influent ClO_4^- level was 310 $\mu\text{g/L}$ and the maximum was 1.1 mg/L. The average nitrate influent level was 6.11 mg/L. The average ethanol feed rate was 3.9 mL/min and was based primarily on the nitrate loading requirements. No unplanned excursions were experienced during the operation of the 52-day FBR pilot test. The system was briefly forced into nutrient-limiting conditions to demonstrate that biological reduction was the primary removal mechanism for ClO_4^- reduction. The elimination of the nutrient supply resulted in gradually increasing levels of ClO_4^- in the effluent from $<4 \mu\text{g/L}$ up to 240 $\mu\text{g/L}$ and nitrate from 0.4 mg/L to 3.32 mg/L over a 10-day period. After this brief test, the ethanol feed rate was returned to the target level and the ClO_4^- effluent levels returned to $<4 \mu\text{g/L}$ and nitrate levels to 0.4 mg/L within one day (Hatzinger et al., 2002). During the pilot test, biomass film growth was managed manually and no problems were reported with

maintaining a stable biomass, or in controlling the bed height or biofilm growth. The pilot test demonstrated that FBR could be successfully implemented at JPL to treat both nitrate and ClO_4^- (U.S. Filter, 2001).

Conclusions

As reported in the GWRTAC report, FBRs are the most commonly studied and/or implemented ex situ biological treatment technology (GWRTAC, 2001). Because FBRs have been successfully implemented at the full-scale at several sites and at the pilot-scale at JPL, it appears that FBR would be the most appropriate reactor configuration for ex situ biological treatment to be implemented as part of an expanded treatability study. The overall advantages and limitations associated with this technology are provided below:

Advantages

- FBRs have a larger surface area for biomass growth compared to PBRs.
- Higher biomass in FBRs allows reactors to have a smaller volume and footprint compared to CSTRs and PBRs.
- Higher biomass means shorter hydraulic residence times with FBRs compared to CSTRs and PBRs.
- FBR operation is more efficient over the long-term compared to PBRs because fluidization and continuous biomass control minimizes clogging and/or channeling in the reactor.
- Recycling of effluent can lead to more stable influent conditions and better bioreactor performance.
- The FBR technology has been successfully commercialized (e.g., at least two full-scale systems are currently in operation).
- Biological treatment methods are typically less expensive in terms of operation and maintenance costs compared to physical/chemical processes.
- Biological treatment methods typically generate less hazardous waste than physical/chemical processes.

Limitations

- FBRs are reportedly more expensive to build and operate compared to PBRs.
- High recycle rates or total flowrates are required to keep the filter media fluidized and this can increase pumping capital and electricity costs.
- Operational problems have been reported in the literature related to bed media loss, bed height control, and the release of biomass into the effluent.

- Process is reliable, but upsets can occur from suboptimal electron donor dosing, pH changes, temperature changes, or other conditions.
- Loss of biological activity could interrupt operation for several days.

Innovative Amendments and Reactor Types

Several novel amendments and/or bioreactor types have been proposed in the literature and by various vendors. O’Niell et al. (1999) discusses the use of microbial mat and algae bioreactors for ClO_4^- reduction. Eco-Mat Incorporated has developed an attached growth reactor that uses a media called Eco-Link. This sponge like material provides a large surface area for naturally occurring denitrifying bacteria to live and grow. This technology is currently used at the full-scale for nitrate removal in aquariums and at the pilot-scale for ClO_4^- removal at groundwater remediation sites. Batista and Liu discuss the use of a microporous membrane reactor where ClO_4^- diffuses across the membrane and is reduced by an immobilized biofilm growing on the membrane (Batista and Liu, 2001). In addition, a number of recent studies have focused on the benefits of using hydrogen as an electron donor for ClO_4^- reduction (Logan, 1998; Van Ginkel et al., 1998; Giblin et al., 2000; and Rittmann et al., 2002).

The use of a PBR configuration for hydrogen delivery has been tested, but more novel bioreactor configurations have also been proposed including a gas-lift reactor with pumice filter media and a hollow-fiber membrane biofilm reactor (HFMBfR). Giblin et al. was able to demonstrate the reduction of ClO_4^- from 0.740 mg/L in the influent to $<4 \mu\text{g/L}$ in the effluent with hydrogen as the electron donor. However, several problems were encountered with this configuration including non-uniform distribution of biomass in the column, unstable pH conditions, and limited delivery of hydrogen to the bacteria (Giblin et al., 2000). In a gas-lift reactor filled with pumice particles, Van Ginkel et al. (1998) was able to demonstrate nearly complete removal of ClO_4^- , chlorate, and chlorite at residence times varying from 0.2 to 120 minutes (as reported by Logan, 1998). Rittmann et al. has demonstrated successful removal of ClO_4^- in a pilot-scale HFMBfR at the La Puente, California Superfund site. This novel reactor configuration uses a composite membrane, which supports the growth of a thin biofilm across the surface. The pilot modules at the La Puente site each contained 7,000 fibers with approximately 13 m^2 of biofilm surface area. The reactor has been shown to be 100% efficient in supplying hydrogen for the reduction of oxygen, nitrate, and ClO_4^- . ClO_4^- was reduced from 60 $\mu\text{g/L}$ in the influent to 3 $\mu\text{g/L}$ in the effluent and nitrate was reduced from 24 mg/L in the influent to $<0.5 \text{ mg/L}$ in the effluent (Rittman et al., 2002). The primary advantages and limitations associated with the use of hydrogen gas bioreactors in a variety of configurations are as follows:

Advantages

- Hydrogen is the least expensive of the electron donor alternatives.
- Biofouling is minimized because hydrogen does not promote vigorous overgrowth of biomass.
- Hydrogen is nontoxic.
- No residual hydrogen is left in the treated water.

Limitations

- Hydrogen does not promote cell biomass growth, so sustainability of removal rates over time is uncertain.
- Only one pilot-scale field application of the hollow-fiber membrane biofilm reactor has been completed to date.

In Situ Bioremediation

Several authors have noted the potential for bioremediation to effect the in situ treatment of perchlorate-impacted soil and groundwater including Hatzinger et al. (2002), Logan (2001), and others. In situ bioremediation can be used to achieve source area treatment and thereby decrease or eliminate ClO_4^- dissolution into the groundwater over the long term. In situ bioremediation can also be implemented in a biobarrier application to prevent off-site migration of perchlorate-contaminated groundwater. Numerous microcosm studies have been completed that demonstrate the successful biodegradation of ClO_4^- using a variety of electron donor amendments (see Table F-2). In addition, perchlorate-reducing microbes have been shown to be present in a wide variety of environments including pristine and hydrocarbon-contaminated soils, aquatic sediments, paper mill waste sludge, and farm animal waste lagoons (Gingras and Batista, 2002). Despite several successful laboratory studies, only a few in situ bioremediation field-scale applications have been completed to date for ClO_4^- remediation. Based on the results from these initial field tests, the primary challenge appears to be adequate delivery of the electron donor to the subsurface over large source areas and/or in groundwater plumes located at depths greater than 100 ft bgs (Hatzinger, 2002).

In Situ Bioremediation Amendments

Although ClO_4^- is readily biodegraded in laboratory microcosm studies, this process may be limited in the field under “natural” conditions for several reasons. This includes the lack of ClO_4^- reducing microbes at a given site, little to no carbon substrate for microbial growth, high dissolved oxygen levels in groundwater, and/or the presence of other compounds, such as nitrate which are preferentially degraded (Logan, 2001 and Zhang et al., 2001).

Some of these factors may be overcome through the injection of bioremediation amendments such as alcohols, fatty acids, edible oils, sugars, or other substances and/or through the introduction of cultured, perchlorate-reducing microbes (i.e., bioaugmentation). In general, bioaugmentation is not necessary because most perchlorate-contaminated sites have been demonstrated to contain indigenous populations of ClO_4^- reducing microbes and bioaugmentation has not been demonstrated to substantially increase ClO_4^- degradation rates in microcosm studies (Coates, 2000). As shown in Table F-2, several amendments have been tested for their ability to promote the biodegradation of ClO_4^- . In general, the amendment is used by the microorganisms to build cell biomass and acts as an electron donor through oxidation to carbon dioxide and water. ClO_4^- acts as the electron acceptor and is sequentially reduced to chlorate, chlorite, and then chloride and oxygen (Cox, 2001). Several confounding factors or parameters can inhibit this process including the presence of oxygen and nitrate, which compete with ClO_4^- as electron acceptors. Low pH (e.g., less than 5) and high salinity levels have also been reported to decrease ClO_4^- biodegradation rates (Hatzinger, 2000; Zhang et al., 2001).

The selection of the most appropriate amendment should be site-specific and is typically based on the biodegradation rates measured in microcosm studies. However, several other issues must be considered

in the selection of an amendment including cost, supply, presence of impurities or nuisance compounds (e.g., sulfur in molasses), and the ability to obtain permission for injection of the substance into the subsurface. Another consideration is whether a soluble amendment (e.g., acetate) is appropriate or an insoluble amendment (e.g., vegetable oil). Several amendments were tested during the JPL microcosm study including acetate, benzoate, ethanol, lactate, hydrogen, methanol, molasses, propane, sucrose, and yeast extract with ethanol. Table F-2 presents the overall results from this study, along with a summary of amendments tested for use during other in situ bioremediation projects. The JPL study demonstrated that acetate, lactate, ethanol, molasses, and yeast extract were the most promising amendments and achieved rapid biodegradation in less than 14 days. The microcosms with these amendments all showed the reduction of ClO_4^- from 310 $\mu\text{g/L}$ to non-detect ($<4 \mu\text{g/L}$) levels in a rapid time frame. The microcosm study at JPL also demonstrated that indigenous bacteria at the site are capable of reducing ClO_4^- and identified the microbes cultured from the site as *Dechlorosoma suillum* strain JPLRND (Hatzinger et al., 2002).

In Situ Bioremediation Delivery Mechanisms

Several different methods have been proposed in the literature for the delivery of electron donor to the subsurface including passive, semipassive, and active injection scenarios. A brief summary of these methods is provided below.

Passive delivery methods rely upon the natural groundwater gradient and dissolution and dispersion to deliver the electron donor into the subsurface. Passive strategies include permeable reactive barriers or the placement of a slow release compound (e.g., vegetable oil or polylactate) in an array of unpumped wells (ITRC, 1998). As discussed below, a permeable reactive barrier filled with gravel and organic amendments (compost and cottonseed meal) was installed at NWIRP McGregor to intercept the seepage of perchlorate-contaminated groundwater into a nearby stream. Depth to groundwater at this site was less than 6 ft below ground surface (bgs) (Perlmutter et al., 2000). In general, permeable reactive barriers are best suited to shallow groundwater sites because of the need to key the barrier into bedrock or a substantial impermeable clay layer and the limits of conventional trenching methods. This technology would be impractical to implement at JPL because the depth to bedrock at JPL is more than 1,000 ft in some areas. Although the use of hydrogen release compound (HRC), a slow release polylactate, has been demonstrated in laboratory studies to degrade ClO_4^- (Logan et al., 2000), no field-scale applications for ClO_4^- treatment were identified. However, numerous field-scale applications of HRC for chlorinated VOC removal exist in the literature (Koenigsberg and Ward, 2000). Vegetable oil has been proposed for ClO_4^- reduction by several authors including Hunter (2001). The GWRTAC report mentions that a pilot-scale test is planned for ClO_4^- plume treatment with edible oils at Edwards Air Force Base, but the results were listed as still pending (GWRTAC, 2001). Also, a radial biobarrier pilot test with the injection of canola oil and oleate was planned at the Aerojet Facility in California. The anticipated radius of influence was 10 ft around each delivery well (Geosyntec, 2001). In general, slow release compounds are more economical for the treatment of shallow aquifers (<100 ft bgs) because of the tight spacing needed for the introduction of viscous or insoluble substances into the subsurface (Hatzinger, 2002).

Table F-2. Examples of In Situ Bioremediation Amendments for ClO₄⁻ Reduction

Author	Scale	Amendment(s)	Initial [Final] ClO ₄ ⁻ Levels	Initial [Final] Nitrate Levels	Initial [Final] O ₂ Levels	pH	Comment
Hatzinger et al., 2000 and 2002	L	Acetate, Lactate, Ethanol, Molasses, Yeast Extract	310 µg/L [<5 µg/L]	18.6 mg/L	2.6 mg/L	7.6	JPL microcosm results indicate rapid ClO ₄ ⁻ biodegradation (<14 days to ND).
Hatzinger et al., 2000 and 2002	L	Hydrogen, Propane, Methanol, Sucrose	310 µg/L [<5 µg/L]	18.6 mg/L	2.6 mg/L	7.6	JPL microcosm results indicate slow ClO ₄ ⁻ biodegradation rate (~ 21 days to ND).
Zhang et al., 2001	L	Lactate	100 mg/L [ND to 60 mg/L]	13 to 65 mg/L [NA]	NA	NA	ClO ₄ ⁻ degradation rate 33 to 187 µg/day
McMaster and Cox, 2001	P	Acetate	10 to 15 mg/L [<4 µg/L]	5 mg/L [NA]	2 to 5 mg/L [~ 1 mg/L]	NA	Closed loop system. ClO ₄ ⁻ Half-Life 0.2 to 1.8 days. Other substrates tested molasses, canola oil
Hunter, 2001 and 2002	L	Soybean Oil	20 mg/L [0.070 mg/L]	20 mg/L [ND]	NA	NA	$>99\%$ removed between 5 th and 18 th weeks.
Perlmutter et al., 2001	L	Acetate, Molasses	1,500 mg/L [<4 µg/L]	NA	NA	NA	ClO ₄ ⁻ removal rates from 200 to 600 mg/L/day.
Perlmutter et al., 2001	L	Fruit Juice, Compost	1,500 mg/L [NA]	NA	NA	NA	None. Fermentation and lack of organic carbon inhibited degradation.
Arcadis Geraghty and Miller, 2001	P	Corn Syrup	81 to 190 µg/L [18 to 200 µg/L]	13 mg/L	0 to 18.7 mg/L	4.6 to 8.3	Injection with downgradient extraction (~ 400 ft). Also considered molasses, cheese whey.
Logan et al., 2000	L	Hydrogen Release Compound	165 mg/L [<4 µg/L]	NA	NA	NA	Cell growth rates ranged from 3 to 35 hrs
Geosyntec, 2002	P	Calcium Magnesium Acetate	6 to 8 mg/L [5 to 6 mg/L]	NA	5 mg/L [5 to 6 mg/L]	NA	Vadose zone flushing and groundwater treatment. No treatment effected.
Geosyntec, 2001	L/P	Canola Oil and Oleate	100 mg/L [<18 µg/L]	NA	NA	NA	Radial biobarrier. Half-life 2.8 days with canola oil and 5.2 days with oleate.

Semipassive delivery strategies consist primarily of injection-only configurations. These methods rely upon continuous or periodic forced injection of the electron donor into one well or an array of wells. Semipassive systems are best suited to the reduction of chemical concentrations in low-concentration plumes and/or to act as a biobarrier or “polishing step” for other remediation methods. Semipassive systems do not provide hydraulic containment and may produce localized mounding depending upon the injection strategy (ITRC, 1998). Another type of semipassive system is gas injection. Hydrogen, propane, or other gasses can be injected into a contaminated aquifer (typically using a horizontal well configuration). Although, no field-scale applications of gas injection for ClO_4^- plume treatment were identified, this strategy has been used at several sites for chlorinated VOC plume treatment. For example, methane and air were injected at a rate of 250 to 300 cubic ft per minute in a horizontal well to effect chlorinated VOC removal in groundwater at the Former Naval Ammunition Depot in Hastings, Nebraska (ITRC, 1998).

Active methods involve both injection and extraction to promote mixing and delivery of the electron donor in the aquifer. Active delivery methods include dual vertical well recirculation, dual horizontal well recirculation, single vertical well recirculation, and other approaches. Typically, a system will consist of a row of upgradient vertical injection wells paired with a row of vertical downgradient extraction wells. Groundwater is extracted from the downgradient wells, the electron donor is added, and the groundwater is reinjected in the upgradient wells. The injection and extraction wells are most often oriented perpendicular to the natural groundwater gradient, but can be rotated at some angle to allow for the flow of upgradient groundwater through the treatment zone. Vertical wells are the most frequently used, but horizontal wells and trenches can also be employed for injection or extraction. The recirculation of groundwater should promote the mixing of the amendment within the aquifer and will allow for multiple passes of the contaminated groundwater through the treatment zone. Active delivery mechanisms are best suited for treating high-concentration plumes or source areas and can also be designed to provide for hydraulic containment (ITRC, 1998). As discussed below, active delivery systems have been used at Aerojet in Rancho Cordova, California for ClO_4^- plume treatment at depths of 200 ft bgs (McMaster and Cox, 2001; Cox, 2002). In addition, McCarty et al. (1998) has proposed an innovative recirculation cell configuration for the treatment of a chlorinated VOC groundwater plume. The system is designed so that groundwater is never brought to the surface. Instead, a subsurface system is used in which two vertical wells with extraction and injection ports separated by an aquitard are used to recirculate groundwater between two different aquifer layers (McCarty et al., 1998).

Permeable Reactive Barrier Case Study at NWIRP McGregor

An interim stabilization action was needed at NWIRP in McGregor, TX in order to control and prevent off-site migration of perchlorate-contaminated groundwater. ClO_4^- was present in surface water at the site boundary at levels up to 5,600 $\mu\text{g/L}$ and in groundwater at levels up to 91,000 $\mu\text{g/L}$. First, a high permeability cutoff and collection trench was installed at the site in order to intercept groundwater prior to off-site migration or seepage into nearby surface water. The initial remedial action plan called for pumping and ex situ biological treatment of the collected groundwater. However, after several successful bench-scale tests, an in situ bioremediation approach was selected instead. A permeable reactive barrier was determined to be feasible at this site because the water table at the site was only 6 ft bgs and the perchlorate-impacted portion of the aquifer was only 10 to 25 ft thick. The existing cutoff and collection trench originally designed for a pump and treat application was then modified. The trench was backfilled with gravel, organic material (e.g., compost and cottonseed meal), and granular activated carbon. The organic material was added to provide a carbon or electron donor source for microbes to reduce ClO_4^- as groundwater moved through the barrier.

First, a bench-scale study was completed to demonstrate the potential effectiveness of in situ bioremediation with a variety of carbon source material. The media tested included compost, canola oil-

coated wood shavings, cottonseed meal, and granular activated carbon. These materials were mixed with gravel, so that the barrier would remain permeable. The gravel content ranged from 90% to 95% of the total media volume. The bench-scale tests involved the use of four PlexiglassTM bioreactors, each 6 inches in diameter and 18 inches tall. The bioreactors were inoculated with microbes from the local POTW. Flowrates ranged from 2 to 8 mL/min during the tests. Compost and cottonseed meal bioreactors performed the best with >99% and >98% ClO_4^- removal, respectively. In addition, both of these materials contain high levels of nitrogen, which is a key nutrient for microbial growth. Canola-oil-coated wood shavings removed >98% of the ClO_4^- in the influent stream. However, it was determined that the lower levels of nitrogen and phosphorous in the canola oil would make it less effective over the long term compared to compost and cottonseed. Influent ClO_4^- levels in the compost, cottonseed meal, and canola oil reactors ranged from 2,500 $\mu\text{g/L}$ to 8,500 $\mu\text{g/L}$. Effluent ClO_4^- levels in the compost reactor ranged from <4 $\mu\text{g/L}$ to 140 $\mu\text{g/L}$. Effluent ClO_4^- levels in the cottonseed meal reactor ranged from <0.02 $\mu\text{g/L}$ to 310 $\mu\text{g/L}$ and effluent ClO_4^- levels in the canola-oil reactor ranged from <4 $\mu\text{g/L}$ to 480 $\mu\text{g/L}$. The granular activated carbon reactor was shown to have removed only 90% of ClO_4^- during the start of the test and its performance declined over the course of the study as breakthrough occurred.

In order to complete the pilot-scale evaluation, three portions of the existing cutoff and collection trench were modified. The first area consisted of compost at 15% to 20% by volume mixed with drainage aggregate. The second area consisted of granular activated carbon (at 2 lb per foot of trench) placed on top of bedding gravel. The third area consisted of cottonseed placed within the bedding gravel at a rate of approximately 20 lb per ft of trench. Cottonseed meal was then placed on top of the cottonseed at a rate of 2 lb per foot of trench. The system was designed to operate in either a passive mode with the natural groundwater gradient or an active mode with pumping from several lift stations. The active mode could be used as necessary to control the water level in the trench and to promote recirculation of groundwater to increase contact with the trench media.

ClO_4^- levels in the trench prior to startup ranged from 16,000 to 27,000 $\mu\text{g/L}$. Two weeks after media installation, groundwater samples from the trench indicated that anaerobic conditions had been achieved (e.g., ORP <50 mV) and that ClO_4^- had been reduced to non-detect levels (<20 to <100 $\mu\text{g/L}$). Nitrate was also reduced from 15,000 $\mu\text{g/L}$ to non-detect (<50 mg/L). After three months in place, ClO_4^- concentrations in the modified collection trenches were still at non-detect levels. In addition, TCE and 1,1-TCA levels were reduced to below detection limits, with the concentration of daughter products (e.g., 1,2-DCE or 1,1-DCA) increasing in groundwater. Although effective reduction of ClO_4^- , nitrate, TCE, and 1,1-TCA was demonstrated within the trench, downgradient monitoring wells had not yet shown an effect after three months. This was attributed to the low groundwater velocities at the site and the fact that more time would be needed for treated groundwater to reach the downgradient monitoring wells (Perlmutter, 2001).

Recirculation Systems and Biobarrier Case Studies at Aerojet in California

Three successful field-scale demonstrations of in situ ClO_4^- biodegradation have been completed at the Aerojet Facility in Rancho Cordova, California. As part of the Superfund process, several technologies have been tested at this site including several different in situ bioremediation amendments and delivery configurations. The key results from a pilot-scale closed loop recirculation system (5 gpm), a pilot-scale active biobarrier system (20 gpm), and another larger field-scale recirculation system (1,000 gpm) are discussed in following paragraphs.

The ClO_4^- plume at Aerojet originates from a former disposal/burn area. The ClO_4^- plume is approximately 5,000 ft long and 3,000 ft wide in an alluvial aquifer with interbedded silts, sands, and gravel. ClO_4^- levels in the aquifer range from 12 to 15 mg/L. Nitrate levels range from 5 to 24 mg/L.

Sulfate levels are at approximately 10 mg/L. The groundwater is aerobic and oxidizing with dissolved oxygen at 2 to 5 mg/L and ORP ranging from 143 to 263 mV. Chlorinated solvents are also present in the groundwater with TCE levels of approximately 2 mg/L. The impacted aquifer is at a depth of about 100 ft bgs and the groundwater treated during these pilot tests was at depths ranging from 85 to 175 ft bgs. The horizontal hydraulic gradient at the site has been estimated at approximately 30 ft/day and the vertical gradient at 3 ft/day. The groundwater plume is currently captured at the site boundary and treated for chlorinated VOCs and ClO_4^- (using ex situ biological treatment with FBRs) prior to reinjection (Geosyntec, 2002).

The first demonstration was a closed loop recirculation system with 65 ft between a paired extraction and injection well. The flowrate of the system was 5 gpm and the total residence time within the treatment zone was approximately 21 days. During the pilot test, acetate was injected in 4 one-hour pulses per day at an average concentration of approximately 50 mg/L. Two monitoring wells were used to measure system performance. The first well was 15 ft away or a travel time of 2.5 days from the injection well according to tracer tests. The second well was 35 ft away or a travel time of 7 days from the injection well. Within 40 days of startup, ClO_4^- levels were reduced from 12 mg/L to $<4 \mu\text{g/L}$ at the first monitoring well. After about 50 days, the ClO_4^- levels at the second well dropped from 15 mg/L to $<4 \mu\text{g/L}$. The half-life for ClO_4^- was estimated to be between 0.2 and 1.8 days. In addition, the groundwater went from aerobic and oxidizing to mildly reducing or slightly oxidizing as a result of electron donor delivery. During the test, the dissolved oxygen levels dropped to less than 1 mg/L and the ORP ranged from -25.6 to 19.7 mV (McMaster and Cox, 2001).

The second pilot-scale system consisted of an active biobarrier configuration with two upgradient extraction wells (10 gpm each) and one downgradient injection well (20 gpm). The system was designed to extract groundwater from the two extraction wells, amend the groundwater with electron donor, and then reinject the treated water into a downgradient injection well. Instead of setting up a recirculation zone with multiple passes of groundwater through a treatment zone, an active biobarrier is created that will reduce ClO_4^- in downgradient groundwater after a single pass.

The active biobarrier system was installed at the site of the first demonstration project. The 8-inch injection well from the first project was retained and two new 6-inch extraction wells were installed at 200 ft on either side of the original injection well. Groundwater modeling results indicated that pumping the extraction wells at 10 gpm each would provide capture of the core of the ClO_4^- plume in the pilot study area and would set up a hydraulic barrier with a total width of 600 ft across the site. The extracted groundwater was then combined, amended with ethanol, and recharged at 20 gpm into the central injection well. Equipment for the system included submersible pumps, on-line monitoring devices for pH, ORP, ClO_4^- , and groundwater flowrate, low-level pump switches for the extraction wells, and a high-level pump switch for the injection well. A metering pump was used to add ethanol to the extracted groundwater. Ethanol was selected because it was found to be the most cost-effective donor for large-scale use and it did not contribute metals, cations, or anions to the groundwater (e.g., like molasses or lactate). During operation, ethanol was added to the subsurface in a pulsed mode with a single one-hour pulse per day at an average ethanol concentration of 50 mg/L. A programmable logic controller (PLC) was used to control and automate the extraction, injection, and amendment delivery. In addition, five 2-inch monitoring wells were installed to assess the performance of the system as listed in Table F-3.

Table F-3. Summary of Key Results from Active Biobarrier Demonstration

Monitoring Well	Distance	Travel Time	Initial [Final] ClO_4^- Levels	Non-detect Date	DO Range ^(a)	ORP Range ^(a)
Well 3601	15 ft down-gradient	NA	7.8 mg/L [<4 $\mu\text{g/L}$]	9 days	0.4 to 4.1 mg/L	-119 to 183 mV
Well 3600	35 ft down-gradient	5 days	7.8 mg/L [<4 $\mu\text{g/L}$]	9 days	0.7 to 1.5 mg/L	-113 to 213 mV
Well 100	65 ft down-gradient	10 days	6.3 mg/L [<4 $\mu\text{g/L}$]	29 days	1.9 to 4.5 mg/L	-130 to 25 mV
Well 3618	100 ft down-gradient	38 days	3.9 mg/L [0.15 mg/L]	Not ND after 72 days	0.8 to 2.7 mg/L	10 to 185 mV
Well 3617	50 ft cross-gradient	5 days	8.0 mg/L [<4 $\mu\text{g/L}$]	20 days	0.5 to 4.1 mg/L	-102 to 214 mV

Note: DO and ORP range from Day One of test forward.

Table F-3 also summarizes some of the key results from the study. Prior to testing at the site, the aquifer was aerobic and oxidizing with dissolved oxygen at 2 to 5 mg/L and ORP ranging from 143 to 263 mV. The pH ranged from 6.88 to 7.20. Within 6 to 9 days of system startup, the ORP declined and stabilized over the duration of the test at -50 to -100 mV up to 65 ft away from the injection well. Dissolved oxygen decreased to levels below 1 mg/L within 35 ft of injection. ClO_4^- was rapidly reduced during the test as shown in Table F-3. ClO_4^- was reduced to non-detect (<4 $\mu\text{g/L}$) within 29 days at a distance of up to 65 ft downgradient from the injection well. The ClO_4^- half-life was estimated at 0.5 to 1.2 days and was comparable to the results from the first demonstration at 0.2 to 1.8 days (McMaster and Cox, 2001). Several other monitoring parameters were tracked during the pilot test including chloride, nitrate, TCE, and ethanol concentrations in the groundwater. Chloride levels in groundwater were shown to increase slightly from 35 mg/L to 37 to 39 mg/L as ClO_4^- was degraded. Nitrate was reduced from 23 mg/L to less than <0.5 mg/L within 6 to 9 days at distances up to 65 ft downgradient of the injection well. The half-life for nitrate was estimated to be 0.6 to 0.7 days. In addition, rapid and complete dechlorination of TCE to ethene was demonstrated within 35 to 65 ft of the injection well. The calculated half-life for TCE to ethene was 11 days. The ethanol injected into the subsurface was completely depleted within 100 ft of the injection well. The only adverse impact to groundwater noted during the test was the mobilization of low levels of manganese at 1 mg/L. Some operational difficulties were also experienced with the injection well. During the first month of operation the water levels in the injection well rose over time (~20 ft). A chlorine dioxide system was installed after one month to control biofouling in the injection well. Chlorine dioxide was periodically pulsed into the system at concentrations of 29 to 88 ppm over 0.7 to 2.5 hour periods. Approximately nine chlorine dioxide injections were performed over the four months of operation. Despite treatment, injection flowrates were impacted by biofouling and had to be reduced from 20 gpm to 8 to 14 gpm towards the end of the test. However, the water levels were relatively stable in the extraction wells and did not show any clogging from mobilized aquifer fines or other factors (Geosyntec, 2002).

The third demonstration project at Aerojet relied upon modification of a pre-existing pump and treat system. The extracted groundwater was treated for chlorinated VOCs (~ 2 mg/L influent) prior to reinjection into the aquifer. Instead of an ex situ treatment system for ClO_4^- , ethanol was added as an electron donor and the groundwater was reinjected in the subsurface at depths of 125 to 175 ft bgs. The reinjected groundwater contained ClO_4^- at levels up to 250 $\mu\text{g/L}$. It was also saturated with dissolved oxygen at 8 mg/L and had nitrate levels of approximately 9 mg/L. Five reinjection wells are used to recharge the aquifer at 1,000 gpm or approximately 200 gpm per well. After approximately one month of

operation, ClO_4^- levels were non-detect at a monitoring well that was 75 ft away from injection point. During this demonstration, biofouling control was also found to be crucial to effective system operation. One injection well without biofouling control experienced an increase in water levels of about 20 ft, while another well with biofouling control showed an increase in water levels of less than 5 ft (Cox, 2002).

Conclusions

Several factors are important in determining if in situ bioremediation is feasible at a given site including: the depth to groundwater, the aerial extent of the groundwater plume, aquifer geochemistry, the presence of other chemical constituents, the need for hydraulic control, economics, regulations, and other issues (Hatzinger, 2000). ITRC notes that one of the most important criteria in deciding if in situ bioremediation is appropriate is the hydraulic conductivity of the aquifer. In situ bioremediation is best suited to sites with hydraulic conductivities ranging from 10^{-5} cm/s to 1 cm/s. Amendment delivery may be difficult at sites with very low hydraulic conductivities (e.g., less than 10^{-4} cm/s). In addition, sites with very high hydraulic conductivities (e.g., $>10^{-1}$ cm/s) may require high pumping and injection rates to achieve hydraulic containment and/or to provide effective amendment delivery (ITRC, 1998).

The aquifers at JPL are sandy with some intermittent silty layers. Estimated hydraulic conductivities range from 2.1 to 9.5 ft/day or 7.4×10^{-4} to 3.4×10^{-3} cm/s. In situ bioremediation seems to have potential at JPL given the fact that perchlorate-reducing microbes are present in the aquifer and that relatively rapid biodegradation rates have been demonstrated in site-specific microcosm studies with the addition of a variety of electron donors. However, due to the depth of groundwater contamination at JPL, the primary challenge will be to find a cost effective means to deliver the electron donor. The most elevated ClO_4^- concentrations at JPL are present in the first hydrostratigraphic layer (defined as 18 to 280 ft bgs). The primary advantages and limitations associated with the use of in situ bioremediation are as follows:

Advantages

- In situ bioremediation can be used to treat ClO_4^- hot spots that serve as a long-term source to groundwater.
- In situ bioremediation can be used to set up a biobarrier to prevent off-site chemical migration.
- In situ bioremediation destroys ClO_4^- and does not just concentrate it into a brine as with physical methods.
- At some sites, in situ bioremediation can be configured so that no aboveground treatment and/or disposal of groundwater is needed.
- At sites with shallow groundwater and/or a small aerial extent, semi passive or passive delivery methods may involve less capital and operation and maintenance costs compared to ex situ treatment options.
- Chlorinated VOCs (e.g., PCE and TCE) may also be degraded with electron donor delivery to the subsurface.

Limitations

- The number of field-scale applications conducted to date is limited.
- In situ bioremediation is best suited to sites with well-defined source areas and shallow or narrow zones of contamination.
- Biofouling can cause significant operation and maintenance issues over the long-term.
- Inefficient donor delivery can lead to little or no in situ biodegradation of ClO_4^- .
- Low pH, high salinity, and the presence of other compounds (e.g., nitrate) can influence the rate and extent of ClO_4^- degradation.
- In situ bioremediation can adversely impact groundwater quality (e.g., metals mobilization, sulfide release, methane production), so care should be taken to minimize these effects in drinking water aquifers.
- Regulatory approval must be received for amendment injection and/or groundwater reinjection.

Potential physical treatment methods reported in the literature for ClO_4^- include ion exchange, various membrane processes, and granular activated carbon adsorption.

Ion Exchange

Ion exchange involves removing ions from solution through sorption onto a resin. These resins contain positively charged adsorption sites onto which exchangeable anions (typically chloride) are bound. As contaminated groundwater is passed through the resin, ClO_4^- and other anions are sorbed to the resin. The chloride is then released into the effluent stream. The resin eventually becomes saturated with ClO_4^- and other anions such as nitrate and sulfate and must be regenerated. In the regeneration step, a sodium chloride brine is passed through the spent resin and displaces the adsorbed ClO_4^- and other anions from the resin. The ClO_4^- and other anions transferred into the brine solution must then be treated before disposal. A single resin can be regenerated several times before it is spent. Ion exchange concentrates, but does not destroy ClO_4^- , which means that several challenges exist related to brine generation, treatment, and disposal. The waste brine from ion exchange is often very difficult to treat because it can contain very high ClO_4^- concentrations, up to 6 wt% salts, and caustic components. If inexpensive ion exchange resins are used, it is sometimes more cost-effective to incinerate them rather than to pay to treat the regenerant brine (Gingras and Batista, 2002). If regeneration is needed, several authors have proposed ClO_4^- removal through biological treatment or catalytic reduction of the brine (e.g., Gingras and Batista, 2002; Aske, 2002).

Several types of ion exchange resins exist, including weak acid cation (WAC), weak base anion (WBA), strong acid cation (SAC), and strong base anion (SBA) resins and the proper resin is selected based on the type of ion targeted for removal. The goal of resin selection for ClO_4^- removal is to identify a resin that is both highly selective towards ClO_4^- , but is still easily regenerated. These are somewhat competing objectives because the more selective the resin, the more difficult it will be to remove the ClO_4^- during regeneration. Both acrylic and styrenic SBA resins have been demonstrated to remove ClO_4^- to low levels. However, only polyacrylic WBA resins have been demonstrated to achieve satisfactory ClO_4^- removal. Both SBA resins (e.g., Amberlite IRA400 Type I, Dowex MSA-1 Type I, Dowex 550A Type I and Ionac A-641 Type I) and WBA resins (IonacAFP-329 and IonacA-305B) were tested at JPL during preliminary groundwater treatability tests. All of the resins tested were shown to remove ClO_4^- to non-detect ($<4 \mu\text{g/L}$) levels (Foster Wheeler, 2000). SBA resins have a higher selectivity for ClO_4^- than WBA resins, but are therefore more difficult to regenerate. The ammonium hydroxide solutions used for WBA resin regeneration may also be more suitable for regenerant biological treatment compared to the very high salinity solutions used in SBA resin regeneration. In addition to SBA and WBA resins, a new class of anion exchange resins called bifunctional resins has been developed that have a very high selectivity for ClO_4^- . These resins have been demonstrated to be five times more efficient at removing ClO_4^- compared to conventional ion exchange resins. However, a special procedure using a FeCl_3 -HCl solution must be used to achieve effective regeneration and bifunctional resins are more expensive than commercially available resins (Gingras and Batista, 2002). Table F-4 contains a summary of the key results from selected ion exchange studies for ClO_4^- removal and a discussion of case studies is provided below.

Characteristics of various commercially available resins

Researchers at the American Water Works Association Research Foundation (AWWARF) investigated various resins which were commercially available for their capabilities for removing Perchlorate and the effects of temperature and other natural surroundings to their functioning (Table 1, Tripp et. al., 2003).

The study demonstrated that the ion-exchange process with partial regeneration and simple waste brine disposal was cost effective for the treatment of perchlorate-contaminated water when compared to the cost of wholesale purchasing. It also demonstrated that brine treatment through a physical-chemical perchlorate and nitrate destruction system had a significant impact on the cost of the treatment, even though the salt usage costs associated with the brine treatment and reuse options were reduced by approximately 75%. This was because the overall Operation and maintenance cost went up because of the high costs associated with the need for Nanofiltration process for sulfate removal. This made the researchers assess the needs for biological treatment of the brine for reuse options, which proved to be more economical than the physical/chemical processes (Tripp et. al., 2003).

Researchers also encountered a decrease in perchlorate selectivity with the rise in temperature which led them to make a conclusion that during regeneration the temperature of the resin can be raised which can make the resin less selective and so most of the perchlorate can be removed from the resin by the brine spiked with sodium chloride. Therefore, regeneration at higher temperatures was found to be more efficient, and less chloride was required to remove the perchlorate (Tripp et. al., 2003).

One of the major outcomes of the study was that a highly perchlorate selective resin (Ionac SR-7) should be used for the best results. Polystyrene resins can also be used but the problem is the production of N-nitrosodimethylamine (NDMA) within the resin. The state of California currently has a provisional action limit of 20 ng/L for NDMA in drinking water. Therefore, even small amounts produced due to the ion-exchange resins could be a potential problem (Tripp et. al., 2003).

Highly selective anion exchange resins offer considerable advantages over conventional (unselective) resins in the treatment of perchlorate contaminated groundwater. Oak Ridge national Laboratory has developed anion-exchange resins that have a bias for the sorption of large poorly hydrated anions such as perchlorate from contaminated groundwater. Laboratory results at the ORNL indicated that the bifunctional resins, D-3696 (made by Purolite International) and RO-02-119 (prepared at the University of Tennessee-Knoxville), were highly selective toward perchlorate and performed five times better than the best commercial nitrate resin (Purolite A-520 E) and more than an order of magnitude better than some non-selective commercial resins (e.g. Amberlite IRA-900). The bifunctional resins were particularly effective in removing trace quantities of perchlorate in groundwater to below the detection limits (Gu et. al., 1999).

Table F-4: Characteristics of the strong base anion (SBA) resins investigated by various researchers for the AWWARF (Tripp et. Al. ,2003)

Resin Number	Resin Name	Matrix	Functionality	Perchlorate selectivity	Temperature Effect	Manufacturer
1	Duolite A-101D	STY-DVB ^(a)	Q-1 ^(c)	High	Increase in Temperature decreased perchlorate selectivity	Rhom and Haas, Philadelphia, Pennsylvania
2	Duolite ES-171	STY-DVB	Q-1	High	Increase in Temperature decreased perchlorate selectivity	Rhom and Haas, Philadelphia, Pennsylvania
3	Duolite ES-181	STY-DVB	Q-1	High	Increase in Temperature decreased perchlorate selectivity	Rhom and Haas, Philadelphia, Pennsylvania
4	Ionac ASB-1	STY-DVB	Q-2 ^(d)	High	Increase in Temperature decreased perchlorate selectivity	Sybron Chemicals, Pittsburgh, Pennsylvania
5	Ionac ASB-2	STY-DVB	Q-2	High	Increase in Temperature decreased perchlorate selectivity	Sybron Chemicals, Pittsburgh, Pennsylvania
6	Ionac SR-7	STY-DVB	TPA ^(e)	Higher than other Polysterene resins, highest among all the resins	Increase in Temperature decreased perchlorate selectivity	Sybron Chemicals, Pittsburgh, Pennsylvania
7	Lewatit OC-1950	STY-DVB	Q-1	High	Increase in Temperature decreased perchlorate selectivity	Leverkusen, Germany
8	Amberlite IRA-400	STY-DVB	Q-1	High	Increase in Temperature decreased perchlorate selectivity	Rhom and Haas, Philadelphia, Pennsylvania
9	Amberlite IRA-402	STY-DVB	Q-1	High	Increase in Temperature decreased perchlorate selectivity	Rhom and Haas, Philadelphia, Pennsylvania

Table F-4: Characteristics of the strong base anion (SBA) resins investigated by various researchers for the AWWARF (Tripp et. al. ,2003) (Continued)

Resin Number	Resin Name	Matrix	Functionality	Perchlorate selectivity	Temperature Effect	Manufacturer
10	Amberlite IRA-404	STY-DVB	Q-1	High	Increase in Temperature decreased perchlorate selectivity	Rhom and Haas, Philadelphia, Pennsylvania
11	Amberlite IRA-458	Acrylic	Q-1	Low	Not much change	Rhom and Haas, Philadelphia, Pennsylvania
12	Amberlite IRA-900	STY-DVB	Q-1	High	Increase in Temperature decreased perchlorate selectivity	Rhom and Haas, Philadelphia, Pennsylvania
13	Amberlite IRA-958	Acrylic	Q-1	Low	Not much change	Rhom and Haas, Philadelphia, Pennsylvania
14	Amberlite IRA-996	STY-DVB	TEA ^(f)	High	Increase in Temperature decreased perchlorate selectivity	Rhom and Haas, Philadelphia, Pennsylvania
15	Reillex HPQ	PYR-DVB ^(b)	Methylpyridine	High	Increase in Temperature decreased perchlorate selectivity	Reily Enterprises, Indianapolis, Indiana
16	Reillex B-1	PYR-DVB	Benzylpyridine	Higher than the other polyvinyl pyridine resins	Increase in Temperature decreased perchlorate selectivity	Reily Enterprises, Indianapolis, Indiana
17	Reillex DP-1	PYR-DVB	Dipyridine	High	Increase in Temperature decreased perchlorate selectivity	Reily Enterprises, Indianapolis, Indiana

(a) STY-DVB: Polystyrene-divinylbenzene polymer

(b) PYR-DVB: Polyvinylpyridine-divinylbenzene polymer

(c) Q-1: Quaternary amine, type I

(d) Q-2: Quaternary amine, type II

(e) TPA: Tripropyl amine

(f) TEA: Triethyl amine

Case Study: Comparison of the perchlorate selectivity of the Bifunctional resins with the commercially available resins

Highly selective Bifunctional anion exchange resins offer considerable advantages over conventional (unselective) resins in the treatment of perchlorate (ClO_4^-) contaminated groundwater. B. Gu et. al. at the Oak Ridge National Laboratory (ORNL) investigated anion-exchange resins which were all based on a poly (vinylbenzyl chloride) backbone, cross-linked with divinylbenzene (DVB), which contains chloromethyl reaction sites that were functionalized by reaction with various trialkylamine groups to create quaternary ammonium strong-base exchange sites. A systematic study was performed to evaluate the effects of different trialkyl functional groups (or their combinations) in the resin, as well as the percentages of DVB cross-linking, on the resin's selectivity for sorption of ClO_4^- . All synthetic resins were prepared in the laboratory of Professor Spiro Alexandratos of the Department of Chemistry, University of Tennessee, Knoxville. A commercial scale-up version of one of Prof. Alexandratos' resins was prepared to specifications provided by the ORNL investigators by Purolite International (Purolite[®] D-3696). Three commercially-available anion-exchange resins were also selected for investigation, and the performance of these resins formed a benchmark that was the basis for comparison with the new resins. These commercial resins were Purolite[®] A-520E (a resin with triethylamine exchange sites), Sybron Ionac SR-6 (a resin with tributylamine exchange sites), and Amberlite[®] IRA-900 (a resin with trimethylamine exchange sites). (Gu et. al., 1999)

Perchlorate sorption on synthetic resins was determined by bringing 0.1g resin (dry weight equivalent) of ion exchange resin in contact with a solution containing a varying amount of ClO_4^- (100 ml of test solution). The test solution was a stimulant of a typical contaminated groundwater found in Redlands, California and also a sample of groundwater contaminated with ClO_4^- obtained from CrimSouth well, Redlands, California. (Gu et. al., 1999)

Process Description

Laboratory column flow-through experiments were performed using small glass chromatographic columns (10 X 40 mm). Resins were wet packed into the columns and the solution was fed into the columns at a constant speed of 30 mL/min. As seen in Figure F-1, for the field trial three pairs of ion-exchange columns (25 X 115 mm glass columns) with different resins were used. The contaminated groundwater was pumped through the column set at a flow rate of ~200 mL/min per column set. The inlet pressure ranged from ~20 to 30 psi and varied slightly in each individual column. The flow rate was kept relatively constant (between 150 and 210 mL/min) by adjusting the inlet pressure (or flow rate) periodically. (Gu et. al., 1999)

The distribution coefficient for sorption of ClO_4^- to the resins, K_d (in mg/L) was calculated as the ratio of ClO_4^- sorbed (expressed as mg per gram of resin) to the concentration of ClO_4^- remaining in solution (mg/mL), that is,

$$K_d = \frac{\text{perchlorate sorbed on the resin (mg/g)}}{\text{perchlorate in solution (mg/mL)}} = \frac{(C_o - C)/m}{C}$$

Where C_o and C are the initial and final concentrations (mg/mL) of ClO_4^- in solution, and m is the mass of resin per unit volume of solution (expressed as g/mL). The apparent distribution coefficient was measured as a function of time, and equilibrium was assumed to be reached when the apparent K_d value no longer changed. (Gu et. al., 1999)

Results and Discussion

Results from the column studies indicated that the ORNL-developed bifunctional resins were much more selective toward ClO_4^- (K'_d values were 2 - 5 times higher) than the two commercial resins (Purolite[®] A-520E and Sybron Ionac[®] SR-6). At an initial concentration of ~ 1 mg/L ClO_4^- the bifunctional resins removed the ClO_4^- in solution to below the detection limit (~ 0.003 mg/L) within 1 h. The synthetic monofunctional resin VP-02-152 (tripropylamine resin) reduced the perchlorate to below detection limits within 24 h. On the other hand, the commercial resins Purolite[®] A-520E and Sybron Ionac[®] SR-6 took ~ 1 week to remove ClO_4^- below the detection limit. The laboratory scale study thus led to the conclusion that the bifunctional resins are particularly effective in removing trace quantities of ClO_4^- in aqueous solution as it is commonly encountered under natural groundwater conditions. (Gu et. al., 1999)

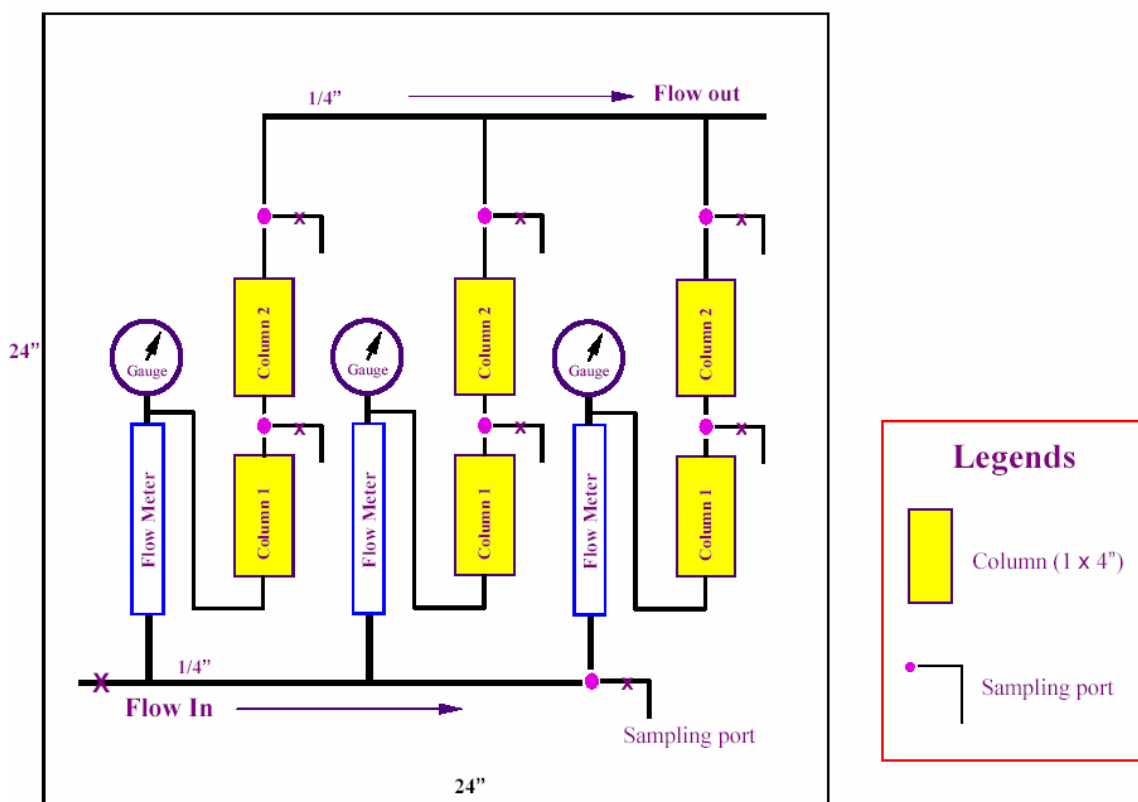


Figure F-1: Design of the field experiment for the flow-through column testing (Gu et. al., 1999)

Results from the small-scale field test indicated that the bifunctional synthetic resin (D-3696) prepared by Purolite for ORNL performed ~ 5 times better than the best commercial nitrate-selective resin (Purolite[®] A-520E). Breakthrough of ClO_4^- on the Purolite[®] A-520E lead column occurred after $\sim 8,500$ bed volumes of groundwater had passed through the column. On the other hand, ClO_4^- breakthrough occurred at $\sim 40,000$ bed volumes in the D-3696 resin column. In the second column $\sim 3\%$ breakthrough of ClO_4^- occurred at $\sim 22,000$ bed volumes in the Purolite[®] A-520E column but this breakthrough level required $\sim 104,000$ bed volumes in the D-3696 column. At a 10% breakthrough (presumably the remediation target), the bifunctional D-3696 resin was able to treat up to $\sim 112,000$ bed volumes of groundwater containing $\sim 50\mu\text{g/L}$ ClO_4^- (as seen in Table F-5) and running at ~ 2 bed volumes per minute (or at a residence contact time of < 20 s). The best commercial resin (Purolite[®] A-520E, the nitrate selective resin)

treated up to ~24,000 bed volumes of the groundwater under the same experimental conditions. These observations suggested that the bifunctional resin, D-3696, can also adsorb more ClO_4^- than Purolite[®] A-520E after the breakthrough occurs. In other words, the bifunctional resin columns may be configured with a relatively long pass length to enhance its treatment efficiency and longevity. (Gu et. al., 1999)

Table F-5: Major contaminants and chemical properties of groundwater at the experimental field site. (Gu et. al., 1999)

Property	Site groundwater
Cl^- (mg/L)	7.0
NO_3^- (mg/L)	61.2
SO_4^{2-} (mg/L)	14.9
Ca^{2+} (mg/L) ¹	21.7
Alkalinity (mg/L) ¹	98.6
ClO_4^- (mg/L)	0.05
N-NDMA (mg/L) ¹	0.15
Trichloroethylene (mg/L) ¹	0.3
pH	6.9

The groundwater was pumped directly through the resin columns without any pretreatment. This resulted in retention of some dissolved organic matter (DOM) present in the natural groundwater. These organic materials in groundwater are generally negatively charged, so that they can also be strongly adsorbed by the anion exchange resins and may compete with the adsorption of ClO_4^- on the resin beads. The Purolite[®] A-520E appeared to have retained the least amount of DOM by visual comparison of the columns. However, the retention of the DOM did not appear to significantly reduce the performance of the Purolite bifunctional resin to remove ClO_4^- , which may be again attributed to the high selectivity of the bifunctional resins to poorly hydrated oxyanions such as ClO_4^- . These observations suggest that additional cost-savings could be gained by using highly selective synthetic resins in groundwater ClO_4^- -treatment. Unlike the conventional groundwater treatment which normally requires a pretreatment stage to remove or filter DOM and other competing anions (such as SO_4^{2-}) that would otherwise reduce or interfere with the retention and removal of ClO_4^- , the use of highly selective bifunctional resins requires no pretreatment. (Gu et. al., 1999)

Bifunctional Anion Exchange Study at Edwards Air Force Base, CA

A pilot-scale test was conducted at Edwards Air Force Base in California to investigate the use of bifunctional anion exchange resins for the treatment of perchlorate-contaminated groundwater. The primary advantages associated with bifunctional resins include the fact that ClO_4^- is preferentially removed over other common anions in groundwater and that the higher adsorption means the system can be operated with a higher flowrate and/or a smaller volume than conventional ion exchange systems. For the initial phase of the pilot test, both a bifunctional resin (Purolite D-3696) and a monofunctional resin (Purolite A-520E) were run in parallel. Each ion exchange column was 2 inches in diameter and 12 inches in depth and received a flow of groundwater at 500 to 700 mL/min. This flowrate corresponds to about one bed volume per minute. Finally, a third ion exchange column was used as a polishing step to capture any residual ClO_4^- prior to discharge of the treated groundwater. Influent ClO_4^- levels ranged from 400 to 500 $\mu\text{g/L}$ (Gu et al., 2002).

It was demonstrated that initial breakthrough of the monofunctional resin occurred after 14,000 bed volumes, whereas full breakthrough occurred at 35,000 bed volumes. By comparison, initial breakthrough occurred at 20,000 bed volumes for the bifunctional resin and full breakthrough at 56,000 bed volumes. It was estimated that more than 5,400 mg of ClO_4^- was retained in the monofunctional resin, whereas more than 10,700 mg was retained in the bifunctional resin. However, it was discovered that iron oxyhydroxide precipitation and biomass growth had impacted both ion exchange columns and caused clogging, so a second test was conducted with fresh bifunctional resin. A filter (0.5- μm pore size) was added to the inlet of the system to prevent clogging of the new bifunctional resin column. During the second test, the flowrate through the bifunctional resin column was set at 700 mL/min. The performance of the bifunctional resin was significantly improved during the second test. Initial breakthrough did not occur until about 40,000 bed volumes and more than 10,000 mg of ClO_4^- was retained in the resin. The researchers were also able to demonstrate that the spent bifunctional resin bed could be successfully regenerated using the $\text{FeCl}_3\text{-HCl}$ technique recently developed at Oak Ridge National Laboratory. Almost 100% of the sorbed ClO_4^- was recovered with only two bed volumes of regenerant solution. The maximum concentration of ClO_4^- in the regenerant brine was 60,000 mg/L. The regeneration technique involves the use of the tetrachloroferrate anion (FeCl_4^-), which has a stronger affinity for the resin than ClO_4^- . However, this anion can later be decomposed to Fe^{3+} , FeCl^{2+} , and FeCl_2 species that will readily desorb from the resin. Next, the Fe(III) species are washed out of the resin bed using a dilute HCl solution followed by a water rinse. The rinsing step requires about 20 to 30 bed volumes to remove the ferric ions to a low or non-detect level in the effluent (Gu et al., 2002).

Table F-6. Selected Ion Exchange Treatment Case Study Results

Author	Scale	Resin Type	Resin Brand	Column Size	EBCT	Total Flow-rate	Regenerant Type	Regenerant Volume	Initial [Final] ClO_4^- Levels	ClO_4^- Breakthrough	Initial [Final] Nitrate Levels
Najm et al., 1999	L	SBA Polystyrene	Rohm & Hoss IRA400	13 mL Resin Volume	1.5 min	13 mL/min	NaCl (>60 lb/ft ³)	4 Bed Volumes	200 µg/L [<4 µg/L]	7,500 Bed Volumes	9 mg/L [NA]
Najm et al., 1999	L	SBA Polystyrene	Sybron ASB-2	13 mL Resin Volume	1.5 min	13 mL/min	NaCl (30 to 45 lb/ft ³)	4 Bed Volumes	200 µg/L [<4 µg/L]	6,000 Bed Volumes	9 mg/L [NA]
Najm et al., 1999	L	SBA Polyacrylic	Rohm & Hoss IRA458	13 mL Resin Volume	1.5 min	13 mL/min	NaCl (30 to 45 lb/ft ³)	4 Bed Volumes	200 µg/L [<4 µg/L]	450 Bed Volumes	9 mg/L [NA]
Najm et al., 1999	P	SBA Polyacrylic	Purolite A850	0.062 ft ³	1.5 min	0.3 gpm	NaCl (30 to 45 lb/ft ³)	16 Bed Volumes	90 to 140 µg/L [<4 µg/L]	725 Bed Volumes	6.6 mg/L [NA]
Najm et al., 1999	P	SBA Polystyrene	Sybron ASB-2	0.062 ft ³	1.5 min	0.3 gpm	NaCl (30 to 45 lb/ft ³)	16 Bed Volumes	90 to 140 µg/L [<4 µg/L]	>750 Bed Volumes	6.6 mg/L [NA]
Najm et al., 1999	P	SBA Polyacrylic	Rohm & Hoss IRA458	0.062 ft ³	1.5 min	0.3 gpm	NaCl (30 to 45 lb/ft ³)	16 Bed Volumes	90 to 140 µg/L [<5 µg/L]	560 to 725 Bed Volumes	6.6 mg/L [NA]
Vankatesh et al., 2000	P	SBA Polyacrylic	ISEP ⁺ ™ process	30 small columns	16.6 min	4.28 gpm	NaCl (7 wt%)	0.75% Total Influent Flow	50 to 80 µg/L [<4 µg/L]	NA	22 to 28 mg/L [5 to 14 mg/L]
Vankatesh et al., 2000	P	SBA Polyacrylic	ISEP ⁺ ™ process	30 small columns	16.6 min per column	4.28 gpm	NaCl (7 wt%)	0.16% with PNDM	250 to 1,200 µg/L [<4 µg/L]	NA	15 to 20 mg/L [<2 mg/L]
Gu et al., 2002	P	SBA	Purolite 520E	2 in dia and 12 in length	1 min	500 to 700 mL/min	FeCl ₃ -HCl	6 Bed Volumes	400 to 500 µg/L [<4 µg/L]	14,000 Bed Volumes	0.7 mg/L [NA]
Gu et al., 2002	P	Bifunctional	Purolite D3696	2 in dia and 12 in length	1 min	500 to 700 mL/min	FeCl ₃ -HCl	2 Bed Volumes	400 to 500 µg/L [<4 µg/L]	20,000 to 40,000 Bed Volumes	0.7 mg/L [NA]
Burge and Halden, 1999	L/P	Nitrate Specific	Sybron SR-7	5.0 ft ³ Resin Volume	NA	0.62 /15 gpm	NaCl	2% Total Influent Flow	27 µg/L [<4 µg/L]	NA	100 mg/L [17 to 23 mg/L]

P = Pilot Scale.

L = Laboratory Scale.

Brine Treatment

The brine from regenerating an anion exchange resin bed contains high concentrations of perchlorate as well as high total dissolved solids (TDS). The brine stream may range from 1% to 5% of the volume of contaminated water treated, but is usually in the range of 1% to 2%. Approximately 10 pounds of salt is used to regenerate each cubic foot of resin. Technologies to treat the concentrated regeneration brine include:

Biological brine treatment: The Biological Brine Treatment process employs a closed reactor with multiple taps to introduce spent brine, draw-off treated brine, or simple water quality. The system is operated as a sequencing batch reactor and utilizes a marine sediment inoculum to biologically reduce both perchlorate and nitrate in a three percent brine solution. This system uses acetic acid as an electron donor for the reduction process (Case, 2003).

Physical/Chemical brine treatment: One of the Physical/Chemical brine treatment process has been developed by the Company Calgon Carbon and is called the Calgon ISEP system. This system employs a high-pressure and a high-temperature catalytic process to reduce the nitrate and perchlorate in the spent brine. After treatment, the brine is ready for reuse without additional treatment. The process uses a chemical reductant (ammonia) based on the measured concentrations of nitrate and perchlorate in the spent brine. Even ORNL has developed a method of degrading the perchlorate present in the brine completely to chloride and water using ferrous ion and/or non-toxic organic reducing agents and FeCl_3 -HCl as a regenerant solution (US patent pending) (Case, 2003).

Applied Research Associates- Integrated thermal Treatment Process: Laboratory research demonstrated that perchlorate in regenerant brine could be thermally decomposed at elevated temperature and pressure with the addition of reducing agents and promoters. Concentration of the brine with reverse osmosis would be necessary to make the process cost-effective (US patent pending) (CA EPA, 2004).

Electrolytic brine treatment: A simple bipolar electrochemical cell was developed to electrolytically reduce the perchlorate and/or nitrate present in the spent ion-exchange brine. This process does not require the addition of an electron donor as with the biological process or a reductant as with the physical/chemical treatment process.

A study by the AWWARF has given the costs for some of the different brine treatment processes as:

- Brine Discharge (without perchlorate destruction) = \$1.30/1,000 gallons (\$430/acre-foot)
- Biological brine treatment with reuse = \$1.15/1,000 gallons (\$375/acre-foot)
- Physical/chemical brine treatment with reuse = \$1.45/1,000 gallons (\$465/acre-foot)

Biological Perchlorate Reduction for Ion Exchange Brine Treatment and Reuse

Various ion-exchange resins have been shown to remove perchlorate; disposal of the regenerate brine is economically taxing and without destruction of the perchlorate can lead to future litigation. To overcome this problem a research team comprising of MWH and the University of Houston has focused on evaluating methods of biologically treating spent ion-exchange brine.

Process Description

Designed, constructed and installed within MWH's Mobile Water Treatment Pilot Trailer, the pilot plant included two parallel ion-exchange columns (clear PVC) that could be operated independently in either co or counter-current exhaustion and regeneration. For this study the columns operated in a counter-current mode with up-flow exhaustion and down-flow regeneration. Screens were inserted at the top and bottom of each ion-exchange column to contain the resin in the column during the exhaustion and regeneration modes. The treated water was collected in a clear tank and the spent brine was either wasted or collected in a holding tank to be fed to the brine treatment system. (Gilligly et. al., 2004)

The biological brine treatment system was 208 L (55 gal) closed reactor operated as a sequencing batch reactor with a mixed culture of microorganisms using acetic acid as an electron donor. Ecology studies revealed that the pure cultures that could be developed on a solid media were all facultative, aerobic, nitrate-reducing organisms. None were identified as known human pathogens. One organism consistently seen in Gram stains, but resisted aerobic or anaerobic solid agar culture techniques was a Gram negative vibrio and was suspected to be the salt tolerant perchlorate reducing organism. Once the nitrate and perchlorate are biodegraded, the mixture is settled, filtered and amended with chloride before its reuse as the regenerant solution. (Gilligly et. al., 2004)

Results and Discussion

Field-scale testing of ion-exchange with brine treatment utilized groundwater from an operational La Puente County Valley Water District well with $65 \mu\text{g/L ClO}_4^-$. Testing results demonstrated that the biological brine treatment system was able to consistently reduce the perchlorate and nitrate concentrations in the spent brine to below treatment goals ($<200 \mu\text{g/L ClO}_4^-$) during 20 cycles of operation. The resin was regenerated with a 3 percent NaCl spent brine during the field testing. Within the 20 recycles there was an increasing trend in the concentrations of selected ions in the finished water quality was observed at the end of exhaustion. The particular problem encountered was the rising trend in the nitrate concentration clearly indicating the loss of sites for nitrate and perchlorate removal in the resin. The options suggested by the authors include 1) periodic wasting of the brine and the treatment to be continued with a fresh batch of brine 2) periodic wasting of small portion of the recycled brine and subsequently amend it with virgin sweet brine to limit the accumulation of other anions too 3) further processing of the brine like passing it through an Nanofiltration membrane. (Gilligly et. al., 2004)

Bench Scale Testing found that a brine solution with 6-8 % NaCl was good enough to completely remove the perchlorate in the solution. The optimal pH was 6-8 for a complete removal and the presence of other anions did not affect the perchlorate removal.(Gilligly et. al., 2004) It is already known that sulfate does not inhibit perchlorate removal by the nitrate or perchlorate selective resins. (Attaway and smith, 1993; Logan, 1998; Coates et. al. 1999)

An engineering cost model developed to determine the cost of brine treatment and reuse indicated that the cost of the ion-exchange process with biological brine treatment was

approximately around \$1.15/1000 gallons and approximately \$1.45/1000 gallons for physical/chemical brine treatment and reuse system. A conventional ion-exchange system with brine discharge (no perchlorate destruction) was estimated to cost \$1.30/1000 gallons. (Gillogly et. al., 2003)

Bruce et. al. at the Pennsylvania State University have also demonstrated that the perchlorate-respiring microorganisms (PRM) can grow in solutions with high salinity, higher than 3% and upto 11%. The samples for perchlorate reduction were obtained from Great Salt Lake, Utah (GSL); salt marsh water, Delaware Bay estuary (DB); bottom sediments (SBS) and surface water (SBW) from a brackish coastal lagoon and a biofilm/sludge mixture from seawater filter system sludge (SBB) from the top of the large sand filter of the university seawater system. GSW and SBL samples demonstrated growth of PRM in highly saline environment also. This work demonstrated the potential of perchlorate contaminated brine solutions. (Logan et. al., 2001).

ISEP⁺™ Case Studies

Calgon Carbon Corporation (Calgon) completed a 5-month pilot test at JPL to test the effectiveness of granular activated carbon (GAC) adsorption for VOC removal paired with Calgon's patented ion exchange process (ISEP⁺™) for ClO₄⁻ removal from groundwater. In addition, the ISEP⁺™ process has been used at a groundwater remediation site in Henderson, Nevada.

The ISEP⁺™ system consists primarily of an ion exchange unit, a perchlorate and nitrate catalytic destruction module (PNDM), a nanofiltration system for sulfate removal from the brine, and a reverse osmosis unit for rinse water treatment. A strong base polyacrylic Type I resin is typically used in this system. Calgon's ISEP⁺™ system is configured to operate in a continuous sequence of ClO₄⁻ adsorption, regeneration, and rinsing. Continuous operation is made possible by a system of 25 to 30 ion exchange columns that are placed on a rotating carousel. Each column is packed with millions of small resin beads. First, the ClO₄⁻ present in the feed water is exchanged with chloride on the resin in the adsorption zone. The influent water is loaded in a downflow configuration from the top to the bottom of the column. The treated effluent from the adsorption zone typically contains <4 µg/L of ClO₄⁻. Next, the resin containing the adsorbed ClO₄⁻ is rotated into the regeneration zone. A brine of sodium chloride is then pumped in an upflow configuration from the bottom to the top of the column. The regenerant flow is split equally and pumped into each column in the regeneration zone in parallel. The spent brine effluent will contain a high concentration of ClO₄⁻ and is sent to the PNDM for ClO₄⁻ and nitrate removal. The PNDM relies upon catalytic destruction and is described in more detail in the section on chemical treatment. After the PNDM unit, the brine effluent is passed through nanofiltration to remove sulfate. The treated brine is then routed to a regenerant storage tank where it can be reused in the regeneration process. The ISEP⁺™ system reduces the volume of water used during the regeneration step both through the use of a counter current regeneration step and the recycling of treated brine from the PNDM back into the process. Finally, in the rinse zone, excess brine is removed from the column before it moves back into the adsorption zone. The rinse wash is treated by a reverse osmosis system. The permeate from the reverse osmosis system is reused again as rinse water and the rejectate is sent to the regenerant storage tank. The overall waste generation from the ISEP⁺™ process is typically less than 0.2% by volume of the total influent flow (Vankatesh et al., 2000).

The objectives of the pilot-scale test at JPL were to demonstrate the successful removal of ClO₄⁻ from groundwater to levels less than 4 µg/L and to minimize the volume of waste produced. The pilot-scale system at JPL contained 30 ion exchange columns and was set for a residence time of 16.6 minutes for each column or 8.3 hours to complete one rotation of the system. During the pilot test, all chlorinated

VOCs were treated to non-detect during pretreatment with the GAC units. Influent ClO_4^- concentrations ranged from 250 to 1,200 $\mu\text{g/L}$ and were treated to non-detect ($<4 \mu\text{g/L}$) in the effluent. Nitrate was treated from 15 to 20 mg/L in the influent to $<2 \text{ mg/L}$ in the effluent and sulfate was treated from 45 to 50 mg/L in the influent to $<2 \text{ mg/L}$ in the effluent. Two brief excursions did occur during testing and were caused by the inadvertent loss of regenerant flow to the system. The PNDM was demonstrated to reduce ClO_4^- concentrations in the regenerant brine from 60,000 $\mu\text{g/L}$ to $<125 \mu\text{g/L}$. The results of the PNDM process are discussed in more detail in the section on chemical treatment with catalysts. During the testing, it was demonstrated that the overall waste generation from the ISEPTM system was only 0.16% by volume of the total influent flow (Calgon, 1999).

At a remediation site in Henderson, Nevada, the ISEPTM system was installed to treat perchlorate-contaminated seep water that was collected to prevent it from draining into Lake Mead. The system was started in 1999, but is reported to have been shutdown due to performance issues with the PNDM module. During full-scale operation, the system influent flowrates varied from 200 to 560 gpm and influent ClO_4^- concentrations range from 80 to 110 mg/L . Typical effluent ClO_4^- levels were reported to be non-detect at $<2 \text{ mg/L}$ as measured with an ion selective electrode (Wagner and Drewry, 2002).

ISEPTM Case Study

A 2,500 gpm ISEP system was installed at the La Puente Valley County Water District in 2000 and is currently operational. It should be noted that the PNDM system was not used at this site because access to a local brine disposal line precluded the need for brine treatment. Use of the treated effluent for potable water distribution was begun in 2001. During pilot-scale testing at this site, it was demonstrated that ClO_4^- in the influent at 50 to 80 $\mu\text{g/L}$ could be treated to non-detect ($<4 \mu\text{g/L}$) in the effluent. Nitrate was removed from 22 to 28 mg/L in the influent to 5 to 14 mg/L in the effluent. Sulfate was removed from 45 to 60 mg/L in the influent to less than 2 mg/L in the effluent. Even without the PNDM unit, the ISEP process only produced regenerant brine at 0.75% by volume of the total influent flow (Venkatesh et al., 2000). Currently, the brine (containing up to 7,000 mg/L of ClO_4^-) is discharged to the nearby industrial brine line. However, brine treatment with biological treatment is being considered and may be implemented within three years due to phasing out of the brine line (Williams, 2002).

Other Ion Exchange Systems

Several vendors offer package ion exchange systems with disposable resins. The West San Bernardino Water District (WSBWD) has one 2,000 gpm U.S. Filter Ion Exchange System and one 2000 gpm Calgon Ion Exchange System. These systems were installed in May of 2003. Each module of the U.S. Filter system consists of two vessels, skid mounted, with all piping, valves, and gauges assembled. Each resin vessel holds 600 ft^3 of resin that needs to be exchanged every 50 to 75 days. The resin is incinerated and the transport and disposal activities are contracted out to U.S. Filter. Some operational issues have been noted including sand accumulation in the resin vessels due to poor well development, bacteria build-up in the resin vessels, and nitrate leakage from the lead resin vessel. Perchlorate has been shown to be removed from 4 to 7 mg/L to non-detect and nitrate from 29 mg/L to non-detect.

Non Regenerable Resins

Dow Chemical Company manufactures DOWEX, anion exchange resin that can be applied as a once through processing tool. The value that a non-regenerated resin method provides is its ability to process large volumes of water while containing the perchlorate for disposal. Resin bound with perchlorate can be completely removed from a site and disposed of in a regulated landfill or sent for specialized incineration (Gisch, 2003).

Conclusions

Although ion exchange for ClO_4^- removal is very effective, the major drawback for its use is the need for treatment and/or disposal of the regenerant brine. For conventional ion exchange systems, the volume of brine generated is typically 2% to 5% of the total influent flowrate. Calgon's ISEP⁺ process has demonstrated only 0.2% of brine production when ion exchange is coupled with catalytic destruction in a PNDM unit. ISEP⁺ is substantially more cost-intensive than biological treatment and performance problems have been reported with the PNDM module at full-scale. Ion exchange was not retained for further consideration for the ETS at JPL because of the higher capital cost for ISEP and the higher operation and maintenance costs for disposable resins. The overall advantages and limitations associated with this technology are provided below:

Advantages

- Existing technology that has been tested at the pilot and full-scale.
- Dedicated commercial vendors and commercially available resins.
- Proven effectiveness at meeting $<4 \mu\text{g/L}$ of ClO_4^- in effluent.
- Physical treatment technologies are more conventional for drinking water applications.

Limitations

- Operation and maintenance costs are typically higher than for biological treatment techniques.
- Not all resins are highly selective for ClO_4^- and other groundwater anions (e.g., nitrate, sulfate) may interfere with its removal.
- Brine treatment and disposal issues may limit cost-effectiveness.

Membrane Processes

Membrane processes include treatment techniques such as reverse osmosis (RO), nanofiltration (NF), and electrodialysis (ED). All of these processes rely upon a semiporous membrane that lets water pass through, but prevents dissolved salts from penetrating the membrane. RO and NF have been reported to achieve more than 80% removal of ClO_4^- from process streams. With all membrane processes, the ClO_4^- removed is not destroyed, but collected and concentrated in a waste brine. The treated effluent that is recovered is referred to as the permeate and the waste brine is referred to as the rejectate. The treated water or permeate must often be remineralized with sodium chloride, sodium bicarbonate, or other salts prior to distribution in drinking water systems to prevent corrosion or other adverse effects (Urbansky, 1999). According to the GWRTAC report, RO and NF are currently being tested for ClO_4^- removal at the laboratory scale by the American Water Works Association Research Foundation (AWWARF) and RO has been tested at the laboratory scale at an unspecified site in Panama City, Florida. Influent ClO_4^- levels for these studies ranged from 8 to 100,000 $\mu\text{g/L}$ of ClO_4^- (GWRTAC, 2001). Reverse osmosis has also been tested at the laboratory scale at JPL as discussed below.

RO Case Study at Jet Propulsion Laboratory in California

U.S. Filter Corporation conducted a laboratory treatability study to assess the effectiveness of using RO to remove ClO_4^- from JPL groundwater. Both a thin film composite membrane and a cellulose acetate membrane were evaluated. Each bench-scale reactor was 2.5 inches in diameter and 40 inches in length with a 23 ft² RO module. The key results from the RO tests are summarized in Table F-7. The results from the thin film composite test were more promising than the cellulose acetate membrane test. In both tests, approximately 80% of the influent stream was recovered as permeate. However, with ClO_4^- influent levels of 800 µg/L, the thin film membrane achieved 12 to 16 µg/L in the permeate, whereas the acetate membrane contained ClO_4^- levels as high as 680 µg/L. The rejectate consisted of 20% of the influent stream and contained ClO_4^- at approximately 3,600 µg/L for the thin film membrane and 1,600 µg/L for the cellulose acetate membrane. The leakage of the cellulose acetate membrane was considered to be unacceptably high, so this membrane was eliminated from further consideration. The rejectate from the thin film experiment was further concentrated by passing it through a second stage RO system. This second stage test indicated that 50% of the original rejectate could be recovered as permeate at ClO_4^- levels of 17 to 18 µg/L. The rejectate from the second stage test contained ClO_4^- at a concentration of 7,900 µg/L. An additional test was conducted using ion exchange as a potential permeate polishing technique. It was demonstrated that non-detect levels of ClO_4^- (<4 µg/L) were achievable when RO permeate samples with up to 38 µg/L of ClO_4^- were applied. Additional experiments were also conducted to show that the RO rejectate could be successfully treated using biological techniques. Although a recovery rate of up to 80% was demonstrated in the laboratory, it was noted that silica levels in JPL groundwater (at 33.1 mg/L) may limit recovery rates during full-scale operation. At an initial recovery of 80%, silica levels in the first pass rejectate would be 165 mg/L. At a second stage recovery of 50%, silica levels would further increase to more than 330 mg/L. These levels are above the solubility threshold and would result in scaling and membrane fouling. To avoid damaging the membranes during full-scale operation, the overall recovery rate would have to be lowered or softening pretreatment would be needed (U.S. Filter, 1999).

Table F-7. Summary of JPL RO Test Results with a Thin Film Composite Membrane

Treatment	Recovery Rate	Amount Recovered	ClO_4^- in Permeate	Rejection Rate	Amount Rejected	ClO_4^- in Rejectate
<i>Thin Film Composite Membrane</i>						
Single Pass RO	80%	80 gpm	12 to 16 µg/L	20%	20 gpm	3,400 to 4,000 µg/L
Second Pass RO	50%	10 gpm	17 to 18 µg/L	50%	10 gpm	7,900 µg/L
Total	90%	90 gpm	12 to 18 µg/L	10%	10 gpm	7,900 µg/L
<i>Cellulose Acetate Membrane</i>						
Single Pass RO	80%	198.1 mL/min	640 to 680 µg/L	20%	787.4 mL/min	1,600 µg/L

Conclusions

The primary advantage of RO treatment is that it is a commercially available technology that has demonstrated effectiveness for ClO_4^- removal. However, it is unlikely that RO would be appropriate for ex situ groundwater treatment at JPL. The cost-effectiveness of this technology is limited both by membrane fouling issues and by the large volume of waste brine that must be treated and/or disposed. At

the JPL site, RO brine production was on the order of 10% of total influent flow compared to 0.2% for the competing ISEPTM process. This treatment approach was not retained for further consideration at JPL.

Granular Activated Carbon Adsorption

GAC adsorption involves the accumulation of chemicals in the aqueous phase onto the solid surface of carbon particles. This accumulation occurs as the attractive forces at the carbon surface overcome the attractive forces of the water. Granular activated carbon is typically an excellent adsorbent due to its high surface area to volume ratio. However, the magnitude of adsorption by GAC is compound specific and several researchers including Cannon and Na (2000) and AWWARF (2001b) have found that ClO_4^- is only weakly adsorbed by GAC and that rapid breakthrough can be expected.

GAC Case Study at Crafton-Redlands Site in California

Cannon and Na (2000) evaluated the ability of GAC to adsorb ClO_4^- at both the field-scale and laboratory scale. They first collected data from 24 GAC contactor vessels that were previously installed at the City of Redlands Texas Street Water Facility to treat chlorinated VOCs. Each vessel contained 20,000 lb of GAC. Twelve vessels were in a lead configuration with each one followed by another GAC vessel in the lag position. The average flow through all of the vessels was 3.6 million gallons per day with a 40-minute contact time in each vessel pair. The groundwater at the site was found to contain between 62 and 138 $\mu\text{g/L}$ of ClO_4^- . Cannon and Na demonstrated that ClO_4^- was being removed by the GAC canisters to non-detect levels ($<4 \mu\text{g/L}$). However, this removal was relatively inefficient. It was determined that in order to sustain ClO_4^- removal, the GAC canisters would have to be changed out every six weeks compared to every eighteen months as necessary for chlorinated solvent removal alone. In addition to the field investigation, several laboratory tests were attempted to improve the adsorptive capacity of GAC and to effect chemical regeneration of the GAC beds in place. Through the preloading of iron and an organic complex solution on the GAC, Cannon and Na (2001) were able to demonstrate an increase of the adsorptive capacity from 0.236 to 0.336 $\text{mg ClO}_4^-/\text{g GAC}$. The authors were also able to restore 50% to 74% of the GAC adsorptive capacity in place by washing it with an anionic reducing compound. The authors predicted that they could extend the life of the carbon by up to 100 days, but this still does not approach the 18-month regeneration time for organic loading alone (Cannon and Na, 2000).

GAC Case Study by AWWARF

As part of an AWWARF study, researchers investigated the ability of granular activated carbon to remove ClO_4^- using virgin GAC, GAC impregnated with Cu and Zn, GAC mixed with solids such as Fe, Zn, and Al, and an ozone-hydrogen peroxide GAC process. The results of the study indicated that ClO_4^- removal could not be attributed to ClO_4^- reduction at the GAC surface, but was due primarily to ion exchange processes. The virgin GAC used in the study was shown to have only a low ion exchange capacity for ClO_4^- (0.172 $\text{mg ClO}_4^-/\text{g GAC}$). The modified GAC experiments also revealed that ion exchange was the primary ClO_4^- removal mechanism. The experiments using ozone and ozone plus hydrogen peroxide indicated that no ClO_4^- reduction had occurred. ClO_4^- treatment was only found to be successful in biologically active carbon with the addition of an electron donor (AWWARF, 2001).

GAC Case Study at Jet Propulsion Laboratory in California

ClO_4^- removal by GAC was tested during the preliminary stages of the JPL groundwater treatability study. The data indicated that adsorption did occur, but to a lesser extent than was observed with ion exchange resins, and that the interim action level (18 $\mu\text{g/L}$ at the time) was not consistently met (Foster Wheeler, 2000).

Conclusions

Due to its low adsorptive capacity for ClO_4^- , GAC is not likely to be an economically feasible alternative for ClO_4^- treatment at JPL. This treatment approach was not retained for further consideration at JPL.

Potential chemical treatment methods reported in the literature for ClO_4^- include chemical reduction, catalytic reduction, electrochemical reduction, photochemical reduction, and precipitation.

Chemical Reduction

According to Urbansky (1999), ClO_4^- cannot be reduced with the chemical compounds commonly used in the water and wastewater treatment industry including thiosulfate ($\text{S}_2\text{O}_3^{2-}$), sulfite (SO_3^{2-}) or elemental metals (e.g., Fe, Zn, Cu). During laboratory treatability testing conducted at JPL, it was demonstrated that ascorbic acid, sodium sulfite, sodium thiosulfite, and sodium dithionite were not able to effect any reduction in a 1 g/L ClO_4^- solution (Foster Wheeler, 2000). Some inorganic species can reduce ClO_4^- in an aqueous solution including titanous ions (Ti^{3+}), molybdenum species ($\text{Mo}[\text{III}]$), and ruthenous ions (Ru^{2+}). However, the kinetics of the reactions are extremely slow (half-lives of hours to days) which makes these processes impractical for implementation in water treatment (Earley et al., 2000). This treatment approach was not retained for further consideration at JPL.

Catalytic Reduction

Catalysts can be used to overcome the high activation energy needed to effect ClO_4^- reduction. Several authors have reported the successful use of a variety of catalyst types for ClO_4^- treatment including Abu-Omar et al. (2000), Earley et al. (2001), and Aske (2002). Four different nickel and palladium catalysts were also tested for their ability to treat groundwater at JPL.

Abu-Omar et al. (2000) reports that recent laboratory studies with rhenium catalysts show promise in achieving ClO_4^- reduction. Abu-Omar et al. tested three different oxorhenium(V) coordination complexes for their ability to reduce ClO_4^- in the presence of sulfides. Using a variety of sulfide substrates, they were able to demonstrate between 57% and 100% removal of ClO_4^- in the presence of the three different catalyst types. The by-products of this process are sulfoxide and chloride (Abu-Omar et al., 2000).

Earley et al. (2001) has patented the use of a titanium catalyst in the presence of ethanol to treat perchlorate-contaminated groundwater (International Patent Number WO 01/14053A1). Earley et al. (2000) reports that the ClO_4^- reduction reaction rate is increased in a less polar ethanol solution compared to the reduction rate in water alone.

Aske (2000) has patented the use of a series of platinum, palladium, and ruthenium catalysts attached to a zirconium dioxide substrate that are capable of treating ClO_4^- , nitrate, and nitrite in groundwater and brine. Either organic reducing agents such as ethanol or acetic acid can be used to facilitate the reaction, or an inorganic reducing reagent such as hydrogen can be used. When organic reducing reagents are used, the primary by-products of this reaction are chlorate, hypochlorite, and chloride, carbon dioxide, and water. During treatability testing of both groundwater and brines, ClO_4^- effluent levels were demonstrated to be consistently below 5 $\mu\text{g/L}$ and nitrate levels below 10 mg/L . Some groundwater may contain enough reductant (in the form of natural organic matter) to facilitate ClO_4^- removal at the levels of 10 to 100 $\mu\text{g/L}$ typically found in groundwater. However, solutions containing ClO_4^- at levels greater than 5,000 $\mu\text{g/L}$ will require an additional supply of reductant such as ethanol, acetic acid, or other compounds.

The catalyst patented by Aske is used in Calgon Corporation's ISEP⁺™ process as part of the PNDM. The ISEP⁺™ process was successfully demonstrated at the pilot-scale at JPL. The PNDM was able to

treat spent brine from the ion exchange units at influent ClO_4^- levels up to 60,000 $\mu\text{g/L}$ and nitrate levels up to 1,000 $\mu\text{g/L}$. The PNDM unit obtained destruction efficiencies exceeding 99.8% and produced non-detectable levels of ClO_4^- in the brine at $<125 \mu\text{g/L}$. Ethanol was used as the reductant at JPL. The reaction rate remained constant at 0.0013 sec^{-1} , which indicates that the JPL groundwater did not contain any potential catalyst poisons (Calgon, 1999).

In addition, during the preliminary stages of the JPL groundwater treatability study, four different metal catalysts were examined for their ability to remove ClO_4^- including a Raney Ni 2400 catalyst, a Raney Ni 2800 catalyst, a Pd/Activated Aluminum catalyst and a Pd/Activated Carbon catalyst. The catalysts were tested at influent ClO_4^- levels of 5 and 50 g/L . No appreciable ClO_4^- removal was observed, with the exception of the Pd-impregnated activated carbon. The low level of ClO_4^- removal achieved during this test was attributed to weak adsorption onto the granular activated carbon rather than ClO_4^- reduction (Foster Wheeler, 2000).

Although catalytic processes seem very promising, there are several drawbacks including the cost of expensive precious metal catalysts and the potential need for effluent pretreatment to avoid catalyst fouling (ESTCP, 2000). Compounds that are known catalyst poisons are iodine, organosulfur, organonitrogen, vanadium compounds, and iron compounds (Calgon, 1999). Although catalysts have been employed at the field scale as part of the ISEPTM process at JPL and other sites, it is unclear whether catalysts would be cost-effective as a stand-alone technology. Catalysts may be more cost-effective when paired with a technology such as ion exchange or reverse osmosis. These processes can concentrate the ClO_4^- influent stream and therefore reduce the volume of water that must be treated in the catalytic unit. Due to the documented higher level of expense compared to biological treatment, this treatment approach (as implemented in the ISEPTM treatment process) was not retained for further consideration as part of an expanded treatability study at JPL.

Electrochemical and Photochemical Reduction

ClO_4^- in an aqueous solution can be reduced to chloride using either electrochemical or photochemical electrode technologies. The American Water Works Association Research Foundation has demonstrated both of these technologies at the laboratory-scale (AWWARF, 2001a). AWWARF researchers tested the use of titanium-dioxide-coated electrodes to apply an electric current directly to perchlorate-impacted water. Other researches have used electrodes coated with platinum, tungsten, carbide, ruthenium, aluminum, and carbon doped with trivalent chromium or aluminum oxide (Urbansky, 1999). The study involved the use of a two-chambered batch reactor system in which the cathodic and anodic chambers were separated by an ion exchange membrane. Initial ClO_4^- concentrations in the study ranged from 50 $\mu\text{g/L}$ to 5,000 mg/L . Reduction of ClO_4^- ranged from 1% at the highest concentration and up to 35% at the lowest concentration. Although electrochemical reduction has been used for metal-plating and brine electrolysis in industry, it is not currently a practical technology for drinking water treatment and further research is needed. Issues include the competition among anions for active sites on the electrode surface (e.g., sulfate and chloride are more strongly sorbed than ClO_4^-) and the fact that the reaction slows with time as chloride sorbs onto the electrode (AWWARF, 2001a). Urbansky (1999) also reports that electrode corrosion, the loss of surface chemical reactivity over time, and natural organic matter adsorption are the primary challenges to full-scale implementation of this technology. AWWARF researchers also tested the use of titanium-dioxide-coated electrodes to reduce ClO_4^- in the presence of ultraviolet light. At an initial concentration of 5,000 mg/L ClO_4^- , photochemical reduction ranged from 4% to 18% (AWWARF, 2001a). In addition, Gurol and Kim (1999) have reported successful reduction of ClO_4^- with metallic iron in the presence of ultraviolet light under anoxic conditions. During their laboratory experiment, more than 99% of ClO_4^- was reduced to chloride. The experiments were carried out in an unbuffered neutral solution with 1,000 $\mu\text{g/L}$ of ClO_4^- and 100 g/L of elemental iron. The UV

intensity ranged from 0.6 to 0.9 W/cm² (Gurol and Kim, 1999). In general, photochemical reduction with electrodes has the same challenges to full-scale implementation as electrochemical reduction (AWWARF, 2001a) and overall, the photochemical reduction process appears to be insufficiently developed and not ready for field-scale project implementation. This treatment approach was not retained for further consideration at JPL.

Precipitation

Chemical precipitation involves the addition of chemicals to convert a soluble compound into an insoluble solid that is subsequently removed by sedimentation or filtration. Urbansky (1998) reports that nitron (C₂₀H₁₆N₄) can be used to precipitate a low solubility nitron-hydrogen ClO₄⁻ salt (HNitClO₄). The solubility of this salt is 0.19 mM. No laboratory or field scale studies of this treatment method were identified and the use of the nitron reagent is reportedly cost-prohibitive (Urbansky, 1998). Mower (1995) has also proposed ClO₄⁻ concentration by water evaporation in a stripping tower and precipitation of ClO₄⁻ with potassium as KClO₄ (U.S. Patent Number 5,382,265). Precipitation methods are typically best suited to the treatment of very highly concentrated wastes and it is not clear that any of these precipitation methods could achieve removal of ClO₄⁻ to levels less than 4 µg/L. This treatment approach was not retained for further consideration at JPL.

Phytoremediation has been suggested as a potential mechanism for degrading perchlorate in soil systems. Phytoremediation may occur by phytoextraction (accumulation in the branches and leaves), phytodegradation, or rhizotransformation (degradation in the root sphere primarily due to microbial activity). Although many plants have shown the ability to accumulate perchlorate, some plants can drive perchlorate degradation completely to chloride. Nzungung and Wang (2000) found that willow trees could degrade 100 mg/L of perchlorate in 53 days, and that minced spinach and tarragon leaves could degrade 7 mg/L of perchlorate in 30 days. There were no lag times for perchlorate degradation in either experiment. Perchlorate degradation by plants was found to occur in two stages (Nzungung and Wang, 2000). The first stage consisted of an initial uptake of perchlorate proportional to the water uptake by the plant, and a slow transformation of perchlorate to chloride in the plant tissues. The second stage was characterized by a rapid removal of perchlorate by degradation in the root zone with little perchlorate taken up (Xu et. al., 2003)

The thermal destruction of ClO_4^- in wastewaters has been studied by Li and Coppola (1999) and Thomason et al. (1995). Thermal treatment was also tested during the preliminary JPL groundwater treatability tests. In a series of laboratory tests, Li and Coppola demonstrated almost complete decomposition of ClO_4^- ions in solution with noncatalytic hydrothermal (high pressure) and thermal (low pressure) treatment methods. For this study, a surrogate ion exchange brine was used as the influent and consisted of a 7 wt% NaCl brine with 800 mg/L of nitrate and 50 mg/L of ClO_4^- . Thermal decomposition testing was conducted in both a continuous-flow reactor system and a batch reactor. Several different amendments were tested for their ability to lower the decomposition temperature and/or their ability to sorb and concentrate ClO_4^- . The amendments tested included ferric and ferrous salts, ferric chloride, carbon, metal oxide, clay, and various polymers. The presence of ferric or ferrous salts was found to reduce the ClO_4^- decomposition temperature to 170°C compared to 600°C without the additive. The other additives tested did not substantially improve the system performance (Li and Coppola, 1999). Thomason et al. (1995) has demonstrated the destruction of ClO_4^- using supercritical water oxidation at approximately 374°C and pressures of 22.1 MPa. Thermal decomposition was also tested during the JPL treatability test using a 100-mL batch of JPL groundwater that was amended with 0.5 g of glucose and boiled for ten minutes. The 5 g/L of ClO_4^- in the groundwater did not thermally decompose during this test (Foster Wheeler, 2000). The temperature at which the sugar water solution began to boil was not reported. The optimal temperature for ClO_4^- decomposition may not have been achieved. In general, the high temperatures and pressures required for successful thermal treatment would likely limit the cost-effectiveness of these approaches at the full-scale. This treatment approach was not retained for further consideration at JPL.

Based on this literature review, only a select number of the available ClO_4^- treatment technologies should be retained for further consideration for the expanded treatability study at JPL. The conclusions of this literature review are as follows:

- It appears that use of the FBR configuration for ex situ biological treatment is favorable given its better track record for effectiveness, reliability, and control as demonstrated by the successful operation of several full-scale groundwater treatment systems and a pilot-scale system at JPL.
- Although the results from numerous in situ biological treatment case studies are encouraging, several issues need to be resolved regarding the application of this technology at JPL. The primary issue is the feasibility of delivering amendments in a cost-effective manner given the aerial extent and depth of the ClO_4^- groundwater plume at JPL.
- Ion exchange is a commercially viable option and may be cost-effective based on site-specific economic considerations. The need for further destruction and/or disposal of the regenerant brine may limit the cost-effectiveness of this option.

REFERENCES

- Abu-Omar, M.M., L.D. McPherson, J. Aria, and V.M. Bereau. 2000. "Clean and Efficient Catalytic Reduction of Perchlorate." *Angew. Chem. Int. Ed.*, 39(23): 4310-4313.
- American Water Works Association Research Foundation. 2001a. *Assessment of the Electrochemical Reduction of the Perchlorate Ion*. AWWA Research Foundation and the American Water Works Association. Denver, CO.
- American Water Works Association Research Foundation. 2001b. *Removal of Bromate and Perchlorate in Conventional Ozone/GAC Systems*. AWWA Research Foundation and the American Water Works Association. Denver, CO.
- ARA, Applied Research Associates
- ARA. 2003. Web Site link available at <http://www.ara.com>.
- ARA. 2000. *Biodegradation of Perchlorate in Reverse Osmosis (RO) Rejectates from Treatment of Groundwater*. Prepared for Foster Wheeler Environmental Corporation, Costa Mesa, CA.
- Arcadis, Geraghty, and Miller. 2001. *Ninety Day Progress Report: Pilot Study of In-Situ Reactive Zone Technology at Aerojet GET B, Rancho Cordova, California*. Prepared for Aerojet in Sacramento, CA. U.S. EPA Region 9 Superfund Records Center No. 1615-02529.
- Aske, J.R. 2002. "Process for Destroying Contaminants in Contaminant Containing Aqueous Streams and Catalysts Used Therefor." United States Patent Number 6,419,837 B1. July 16.
- AWWARF, see American Water Works Association Research Foundation
- Batista, J., and J. Liu. 2001. "Biological Perchlorate Removal from Drinking Waters Incorporating Microporous Membranes." In A. Leeson, B.M. Peyton, J.L. Means, and V.S. Magar (eds.) *Bioremediation of Inorganic Compounds*, Monterey, California. Battelle Press, Columbus, OH. Vol 6(9).
- Burge, S., and R. Halden. 1999. *Nitrate and Perchlorate Removal from Groundwater by Ion Exchange Pilot Testing and Cost Analysis*. Lawrence Livermore National Laboratory, Livermore, CA. UCRL-ID-135639.
- California, EPA, 2004. "Perchlorate Contamination Treatment Alternatives" Report Prepared by the Office of Pollution Prevention and Technology Development, Department of Toxic Substances Control, California Environmental Protection Agency.
- Calgon. 1999. *Final Report for Removal of Perchlorate and Other Contaminants from Groundwater at NASA JPL*. Prepared for NASA JPL, Pasadena, CA.
- Cannon, F.S., and C. Na. 2000. "Perchlorate Removal Using Tailored Granular Activated Carbon and Chemical Regeneration." Presented at the Perchlorate Workshop of the Pollution Prevention Technology Transfer Conference of the Joint Armed Services, San Antonio, TX. August 23-24.
- Case, T., 2003. Perchlorate Removal: Evaluating Treatment options" American Water Works Association Research Foundation Report.

- Clark, R., M. Kavanaugh, P. McCarty, and R.R. Trussel. 2001. *Review of Phase 2 Treatability Study Aerojet Facility Rancho Cordova, California*. Prepared for Aerojet. July.
- Coates, J.D., U. Michaelidou, and S.M. O'Connor. 2000. "The Diverse Microbiology of Per(chlorate) Reduction." *Perchlorate in the Environment*. (Proceedings of the American Chemical Society, Division of Environmental Chemistry Symposium on Perchlorate in the Environment, August 1999). Edited by E.T. Urbansky. Kluwer Academic/Plenum Publishers, NY.
- Cox, E.E., E. Edwards, and S. Neville. 2000. "In Situ Bioremediation of Perchlorate in Groundwater." *Perchlorate in the Environment*. (Proceedings of the American Chemical Society, Division of Environmental Chemistry Symposium on Perchlorate in the Environment, August 1999). Edited by E.T. Urbansky. Kluwer Academic/Plenum Publishers, NY.
- Cox, E.E., M. McMaster, and S.L. Neville. 2001. "Perchlorate in Groundwater: Scope of the Problem and Emerging Remedial Solutions." In *Proceedings of the 36th Annual Engineering Geology and Geotechnical Engineering Symposium*, Las Vegas, Nevada (pp. 27-32). Idaho State UP, Pocatello, ID.
- Cox, E.E. 2002. "In Situ Remediation of Groundwater and Soil Contaminated with Perchlorate and NDMA." *Perchlorate and NDMA in Groundwater: Occurrence, Analysis, and Treatment*. Groundwater Resources Association of California. Baldwin Park, CA. April 17.
- DHS, Department of Health Services
- Department of Health Services. 2002. Letter to D.E. Vanderkar from R.H. Sakajl Regarding Conditional Acceptance of Biological Treatment (Fluidized Bed Reactors) for the Removal of Perchlorate During Drinking Water Production. April 2, 2002
- Earley, J.E., G.A. Amadei, and D.E. Tofan. 2001. "Catalytic System and Method for Reducing Perchlorate Ion." World Intellectual Property Organization Publication Number WO 01/14053 A1.
- Earley, J.E., D.C. Tofan, and G.A. Amadei. 2000. "Reduction of Perchlorate Ion by Titanous Ions in Ethanolic Solution." *Perchlorate in the Environment*. (Proceedings of the American Chemical Society, Division of Environmental Chemistry Symposium on Perchlorate in the Environment, August 1999). Edited by E.T. Urbansky. Kluwer Academic/Plenum Publishers, NY.
- Environmental Security Technology Certification Program. 2000. *ESTCP Cost and Performance Report: Ammonium Perchlorate Biodegradation for Industrial Wastewater Treatment*. Prepared for U.S. Department of Defense. June.
- ESTCP, see Environmental Security Technology Certification Program
- Evans, P., A. Chu, S. Liao, S. Price, M. Moody, D. Headrick, B. Min, and B. Logan. 2002. *Pilot Testing of a Bioreactor for Perchlorate-Contaminated Groundwater Treatment*. In A.R. Gavaskar and A.S.C. Chen (eds.), *Remediation of Chlorinated and Recalcitrant Compounds*, 2002 Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California. Battelle Press, Columbus, OH. ISBN 1-57477-132-9.
- Foster Wheeler. 2000. *Draft Feasibility Study Report for Operable Units 1 and 3: On-Site and Off-Site Groundwater*. Prepared for NASA JPL. January.

- Geosyntec. 2001. *Workplan for a Pilot Test of the Radial Biobarrier Design for In Situ Bioremediation of Perchlorate in Groundwater, Former GET F Sprayfield*. Prepared for Aerojet Environmental Remediation, Rancho Cordova, CA. May. U.S. EPA Region 9 Superfund Records Center No. 1615-02486.
- Geosyntec. 2002. *Final Technical Report for In Situ Bioremediation of Perchlorate Impacted Groundwater*. Prepared for the Strategic Environmental Research and Development Program. June.
- Giblin. T., D. Herman, and W.T. Frankenberger. 2000. "Removal of Perchlorate from Ground Water by Hydrogen-Utilizing Bacteria." *J. Environ. Qual.*, 29: 1057-1062.
- Gingras, T.M., and J.R. Batista. 2002. "Biological Reduction of Perchlorate in Ion Exchange Regenerant Solutions Containing High Salinity and Ammonium Levels." *Journal of Environmental Monitoring*, 4(1): 96-101.
- Gillogly, T., Lehman, G., Lee, A., Clifford, D., Deborah, R., Lin, X., 2003. "Biological, Chemical and Electrolytic Ion Exchange Brine Treatment for Perchlorate and Nitrate Removal" Water Quality Technology Conference, Philadelphia, PA, Nov 2-6, 2003.
- Gillogly, T., Lehman, G., Lee, A., Clifford, D., Deborah, R., Lin, X., 2004. "Biological, Chemical and Electrolytic Ion Exchange Brine Treatment for Perchlorate and Nitrate Removal" Water Quality Technology Conference, Philadelphia, PA, Nov 2-6, 2003.
- Gisch, D., 2003. "Anion exchange resins remove perchlorate from groundwater" *Water and Wastewater International* V 18, n3, p 10.
- Gu, B., Yee-Kyoung, K. and G.M. Brown. 2002. "Treatment of Perchlorate Contaminated Groundwater Using Highly Selective, Regenerable Ion-Exchange Technology: A Pilot-Scale Demonstration." *Remediation* Vol. 12, No. 2, pp. 51-68.
- Gu, B., Brown, G. M., Alexandratos, S.D., Ober, R., and Patel V. 1999. "Selective Anion Exchange Resins for the Removal of Perchlorate from Groundwater" *Report prepared by Oak Ridge National Laboratory* available at clu-in.org/download/contaminantfocus/perchlorate/ORN1.pdf
- Guarini, B. 2002. "Ex-Situ Technologies for the Removal of Perchlorate and NDMA from Water." *Perchlorate and NDMA in Groundwater: Occurrence, Analysis, and Treatment*. Groundwater Resources Association of California. April 17. Baldwin Park, CA.
- Gurol, M., and K. Kim. 1999. "Investigation of Perchlorate Removal in Drinking Water Sources by Chemical Methods." *Perchlorate in the Environment*. (Proceedings of the American Chemical Society, Division of Environmental Chemistry Symposium on Perchlorate in the Environment, August 1999). Edited by E.T. Urbansky. Kluwer Academic/Plenum Publishers, NY.
- Ground Water Remediation Technology Analysis Center. 2001. *Technology Status Report Perchlorate Treatment Technologies*. First Edition. TS-01-01.
- GWRTAC, see Ground Water Remediation Technology Analysis Center.
- Harding ESE. 2001. *Final Phase 2 Treatability Study Report, Aerojet GET E/F Treatment Facility Sacramento, California*. Prepared for U.S. EPA Region 9. September.

- Harding Lawson Associates. 1999. *Final Phase 1 Treatability Study Report: Perchlorate in Groundwater, Baldwin Park Operable Unit, San Gabriel Basin*. Prepared for Baldwin Park Operable Unit Steering Committee. U.S. EPA Region 9 Superfund Records Center No. 47502. April 12.
- Hatzinger, P.B. 2000. *Biotreatment of Perchlorate in Groundwater*. Available at: [https://www.denix.osd.mil/denix/Public/Library/Water/Perchlorate/Technology/Envirogen_Bio_SERDP ppt](https://www.denix.osd.mil/denix/Public/Library/Water/Perchlorate/Technology/Envirogen_Bio_SERDP_ppt).
- Hatzinger, P.B., M.D. Whittier, M.D. Arkins, C.W. Bryan, and W.J. Guarini. 2002. "In-Situ and Ex-Situ Bioremediation Options for Treating Perchlorate in Groundwater." *Remediation*, 12(2): 69-86.
- Herman, D.C., and W.T. Frankenberger Jr. 1999. "Bacterial Reduction of Perchlorate and Nitrate in Water." *J. Environ. Qual.*, 28(May-June).
- Hunter, W.J. 2001. "In Situ Removal of Perchlorate from Groundwater." In A. Leeson, B.M. Peyton, J.L. Means, and V.S. Magar (eds.) *Bioremediation of Inorganic Compounds*, Monterey, California. Battelle Press, Columbus, OH. Vol 6(9).
- Hunter, W.J. 2002. "Remediation of Chlorate Contaminated Water With Barriers Containing Soybean Oil." Submitted for publication in the *Proceedings of The Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California*. May.
- Interstate Technology Regulatory Cooperation Workgroup. 1998. *Technical and Regulatory Requirements for Enhanced In Situ Bioremediation of Chlorinated Solvents in Groundwater*. Available at <http://www.clu-in.org/download/remed/isb-6.pdf>.
- ITRC, see Interstate Technology Regulatory Cooperation Workgroup
- Koenigsberg and Ward. 2000. *Accelerated Bioremediation of Chlorinated Compounds in Groundwater*. Regenesys Bioremediation Products, San Clemente, CA.
- Li, L., and E. Coppola. 1999. *Final Report: Hydrothermal/Thermal Decomposition of Perchlorate. Small Business Innovation Research*. U.S. EPA Grant Number 68D99032.
- Logan, B.E. 2001. "Assessing the Outlook for Perchlorate Remediation" *Environmental Science and Technology*, 35(23): 483-487.
- Logan, B.E. 1998. *A Review of Chlorate and Perchlorate Respiring Microorganisms*. *Bioremediation Journal* 2(2): 69-79.
- Logan, B.E., H. Zhang, J. Wu, R. Unz, and S.S. Koenigsberg. 2000. "The Potential for In Situ Perchlorate Degradation." In G.B. Wickramanayake, A.R. Gavaskar, J.T. Gibbs and J.L. Means (eds.), *Case Studies in the Remediation of Chlorinated and Recalcitrant Compounds*. Battelle Press, Columbus, OH. pp. 87-92.
- Logan, B. E., Wu, J., Unz, R. F. 2001. "Biological Perchlorate Reduction in High-Salinity Solutions" *Water Res.*, Vol. 35, No. 12, pp 3034-3038.

- Losi, M.E., V. Hosangadi, D. Tietje, T. Giblin, and W.T. Frankenberger Jr. 2001. "Bioremediation of Perchlorate in Groundwater and Reverse Osmosis Rejectates." In A. Leeson, B.M. Peyton, J.L. Means, and V.S. Magar (eds.) *Bioremediation of Inorganic Compounds*, Monterey, California. Battelle Press, Columbus, OH. Vol 6(9).
- McCarty, P.L., L.N. Goltz, G. Hopkins, M.E. Dona, J. Allan, B.T. Kawakami, and T.J. Carrothers. 1998. "Full-Scale Evaluation of In Situ Cometabolic Degradation of Trichlorethylene in Groundwater through Toluene Injection." *Environmental Science and Technology*, 32: 88-100.
- McMaster, M.L., and E.E. Cox. 2001. "Successful Field Demonstration of In Situ Bioremediation of Perchlorate in Groundwater." In A. Leeson, B.M. Peyton, J.L. Means, and V.S. Magar (eds.) *Bioremediation of Inorganic Compounds*, Monterey, California. Battelle Press, Columbus, OH. Vol 6(9).
- Mower, G.L. 1995. "Perchlorate Removal Process." U.S. Patent Number 5,382,265. January 17.
- Najm, I., T. Rhodes, L. Boulos, B. Gallagher, R. Bowcock, C. Williams, and C. Dennis. 1999. "Application of Ion-Exchange Technology for Perchlorate Removal from Drinking Water." In: 1999 Annual Conference Proceedings; American Water Works Association, Chicago, IL. June 20-24.
- NZENGUNG, V.A., and WANG, C.H. (2000). Influences on phytoremediation of perchlorate-contaminated water. In E.T. Urbansky, Ed., *Perchlorate in the Environment*. New York: Kluwer Academic/Plenum Publishers, pp. 219-230.
- O'Niell, W., V. Nzungung, and A. Adesida. 1999. "Treatment of Perchlorate Contaminated Water in Microbial Mat, Algae, and EBB-and-Flow Bioreactors." *Case Studies in Remediation of Chlorinated and Recalcitrant Compounds*.
- Perlmutter. 2000. "Concept to Pilot-Scale: Ex Situ Biotreatment of Perchlorate-Contaminated Soil and Groundwater." Air and Waste Management Association, 93rd Annual Conference and Exhibition, Salt Lake City, Utah, June 18-22.
- Perlmutter, M.W., R. Britto, J.D. Cowan, M. Patel, M. Craig. 2000. "Innovative Technology: In Situ Biotreatment of Perchlorate-Contaminated Groundwater." Proc. Air and Waste Management Association, 93rd Annual Conference and Exhibition, Salt Lake City, Utah, June 18-22, 2000.
- Perlmutter, M.W., R. Britto, J.D. Cowan, and A.K. Jacobs. 2001. "In Situ Biotreatment of Perchlorate and Chromium in Groundwater." In A. Leeson, B.M. Peyton, J.L. Means, and V.S. Magar (eds.) *Bioremediation of Inorganic Compounds*, Monterey, California. Battelle Press, Columbus, OH. Vol 6(9).
- Rittmann, B.E., R. Nurenberg, T.E. Gillogly, G.E. Lehman, and S.S. Adham. 2002. "Perchlorate Reduction Using the Hollow-Fiber Membrane Biofilm Reactor." Submitted for the Proceedings of the Seventh International Symposium on In Situ and On-Site Bioremediation, Orlando, FL, June 2003.

- Sutton, P.M., and M. Greene. 1999. "Perchlorate Treatment Utilizing GAC and Sand Based Biological Fluidized Bed Reactors." Water Environment Federation 72nd Annual Conference and Exposition. New Orleans, LA. October 9-13, 1999. p. 1026-1036.
- Thomason, T.B., G.T. Hong, K.C. Swallow, and W.R. Killilea. 1995. "*The MODAR Supercritical Water Oxidation Process*." Innovative Hazardous Waste Treatment Technology Series. Volume 1: Thermal Processes.
- Togna, P.A., W.J. Guarini, S. Frisch, M. Del Vecchio, J. Polk, C. Murray, and D.E. Tolbert. 2001. "Case Study of Ex-Situ Biological Treatment of Perchlorate Contaminated Groundwater." In A. Leeson, B.M. Peyton, J.L. Means, and V.S. Magar (eds.) *Bioremediation of Inorganic Compounds*, Monterey, California. Battelle Press, Columbus, OH. Vol 6(9).
- Tripp, A. R., Clifford D., Roberts, D.J., Cang, Y., Aldrige, L., Gillogly T., Boulos L., 2003. "Treatment of Perchlorate in Groundwater by Ion Exchange Technology" Report prepared for American Water Works Association Research Foundation.
- United States Environmental Protection Agency. 1993. *Nitrogen Control Manual*. Office of Research and Development, Washington, DC. EPA/625/R-93/010.
- United States Environmental Protection Agency. 2001. *Record of Decision for the Western Groundwater Operable Unit OU-3, Aerojet Sacramento Site, Rancho Cordova, California*. Prepared by U.S. EPA Region 9, San Francisco, CA. July 20.
- Urbansky, E.T. 1998. "Perchlorate Chemistry: Implications for Analysis and Remediation." *Bioremediation Journal*, 2(2): 81-95.
- Urbansky, E.T. 1999. "Issues in Managing the Risks Associated with Perchlorate in Drinking Water." *Journal of Environmental Management*, 56(2): 79-95.
- U.S. Filter. 1999. Removal of Perchlorate from Groundwater Using Reverse Osmosis and Biological Treatment. Prepared for Foster Wheeler Environmental Corporation, Costa Mesa, CA.
- Van Ginkel, G.C., A.G. Kroon, G.B. Rikken, and S.W. Kengen. 1998. "Microbial Conversion of Perchlorate, Chlorate, and Chlorite." In: Proceedings of the Southwest Focused Groundwater Conference: Discussing the Issue of MTBE and Perchlorate in Groundwater, pp. 92-95. National Groundwater Association.
- Vankatesh, K.R., E.R. Cobes, D.L. Jennings, and N.J. Wagner. 2000. *Process for the Removal and Destruction of Perchlorate and Nitrate from Aqueous Streams*. United States Patent Number 6,066,257. May 23, 2002.
- Wagner, N., and C. Drewry. 2002. "Commercial Systems Treating Both High and Low Strength Perchlorate Applications Utilizing Ion Exchange. Available at: <https://www.denix.osd.mil/denix/Public/Library/Water/Perchlorate/technology.html>
- Williams, C. 2002. "Solving the San Gabriel Basin Perchlorate Problem." *Perchlorate and NDMA in Groundwater: Occurrence, Analysis, and Treatment*. Groundwater Resources Association of California, Baldwin Park, CA. April 17.

- Xu, J., Song, Y., Min, B., Steinberg, L., and Logan B. 2003. "Microbial Degradation of Perchlorate: Principles and Applications" *Environmental Engineering and Science*, Vol. 20, Number 5, p 405-422.
- Zhang, Z., T. Else, P. Amy, and J. Batista. 2001. "Evaluation of In Situ Biodegradation of Perchlorate in a Contaminated Site." In A. Leeson, B.M. Peyton, J.L. Means, and V.S. Magar (eds.) *Bioremediation of Inorganic Compounds*, Monterey, California. Battelle Press, Columbus, OH. Vol 6(9).

ATTACHMENT F1
PERCHLORATE CONTAMINATION TREATMENT TECHNOLOGIES

Table F1-1: Perchlorate Contamination Treatment Technologies (CA EPA, 2004)

Technology & Vendor Name	Technology Description	Scale/Status	Throughput	Projects	Treatment Effectiveness	Costs
ION EXCHANGE						
Calgon ISEP	System includes multiple anion exchange resins mounted on a turntable attached to a rotating multi-port valve.	Full Scale-Operational	2500 gpm	La Puente Valley, CA	~200 µg/L to < 4µg/L	Capital = \$2 million Operating Cost= \$154/ acre-ft
		Full Scale-Operational	450 gpm	Kerr- McGee, Henderson, Nevada. A calgon ISEP PDM (Perchlorate destruction module) installed and operated for six months. Flow rates varied between 200 to 560 gpm. Maintenance problems caused due to high TDS, hardness and sulfate. Operation was discontinued due to corrosion of heat exchangers	80-100 mg/L to >2 mg/L (D.L. ion specific electrode)	
		Pilot Scale-Planned	4.3 gpm	Baldwin Park, CA.	18-76µg/L to < 4µg/L	
		Full Scale-Planned	7800 gpm	San Gabriel Valley water Company, El Monte, CA		
		Full Scale-Planned	7800 gpm	Valley county water district, Baldwin Park, CA		
		Full Scale-Planned	4000 gpm	City of Pasadena, CA. 3000-3500 gpm system proposed at existing wells next to JPL site; planning stage		
Calgon Anion Exchange	Fixed bed non-regenerable anion exchange resin treatment	Full Scale-Operational	5000 gpm	California Domestic Water company, Whittier, CA; (startup 7/2002)	< 14µg/L to <4µg/L	\$125/ acre-ft.
		Full Scale-Operational	5000 gpm	City of Riverside, Ca, Tippecance Treatment	average value of 6.4 ppb to	

Table F1-1: Perchlorate Contamination Treatment Technologies (CA EPA, 2004) (Continued)

Technology & Vendor Name	Technology Description	Scale/Status	Throughput	Projects	Treatment Effectiveness	Costs
				Facility;(startup 12/02)	4.6 ppb	
		Full Scale-Operational	2000 gpm	City of Riverside, CA, Gage Treatment Facility (startup 5/03)		
		Full Scale-Operational	2000 gpm	West San Bernadino Water district, Rialto, CA (startup 05/03)		
		Full Scale-Planned	4050 gpm	City of Monterey Park, CA (1/04)		
		Full Scale-Planned	7800 gpm	San Gabriel Water Company, El Monte, CA		
		Full Scale-Operational	>300 gpm	Kerr- McGee, Henderson, Nevada. Pumping rates varied between 300 gpm to 600 gpm.	System influent averages around 30 ppm. Effluent discharge varies from <0.5 ppm and 2 ppm.	
		Full Scale-Planned	2000 gpm	Loma Linda, CA.		
US Filter Anion Exchange	Fixed bed non-regenerable anion exchange resin treatment	Full Scale-Operational	1000 gpm	Aerojet, CA, Sacramento GET D facility	200 ppb to < 4ppb	
		Full Scale-Operational	2000 gpm	Aerojet, CA, Sacramento GET B facility	50 ppb to <4 ppb	

Table F1-1: Perchlorate Contamination Treatment Technologies (CA EPA, 2004) (Continued)

Technology & Vendor Name	Technology Description	Scale/Status	Throughput	Projects	Treatment Effectiveness	Costs
		Full Scale-Operational	800 gpm	Aerojet and Boeing (Formerly McDonald Douglas), Sacramento, CA	250 ppb to < 4 ppb	
		Full Scale-Operational	800 gpm	City of Morgan Hill, CA.	<10 ppb to < 4 ppb	
		Full Scale-Operational	2000 gpm	West Valley Water Co., West San Bernadino, CA (startup 005/03)	<10 ppb to < 4 ppb	
		Full Scale-Operational	2000 gpm	City of Rialto, CA (startup 08/03)	<10 ppb to < 4 ppb	
		Full Scale-Operational	3500 gpm	City of Colton, CA (startup 08/03)	<10 ppb to < 4 ppb	
		Full Scale-Constructed	5000 gpm	Fontana Union Water Co., Fontana, CA	15 ppb to < 4 ppb	
		Full Scale-Operational	800 gpm	West San Martin Co., West San Martin, CA	17 ppb to < 4 ppb	
Ion Exchange	Originally designed for nitrate removal, anion exchange system achieves perchlorate removal	Full Scale-Operational	10000 gpm	City of Pomona, CA		
SELECTIVE ION EXCHANGE RESINS						
SYBORN IONAC SR-7	Commercially available regenerable resin					
		Full Scale-Operational	1400 gpd	Lawerence Livermore Laboratory- Building 815 SR-7	10 µg/L to < 4 µg/L	
		Full Scale-Operational	5000 gpd	Lawerence Livermore Laboratory- Building 830 DISS	11 µg/L to < 4 µg/L	
		Full Scale-Operational	1000 gpd	Lawerence Livermore Laboratory- Building 854-PRX	7.2 µg/L to < 4 µg/L	
Purolite A-520 E	Commercially available	Lab Study		Paducah gaseous Diffusion		

Table F1-1: Perchlorate Contamination Treatment Technologies (CA EPA, 2004) (Continued)

Technology & Vendor Name	Technology Description	Scale/Status	Throughput	Projects	Treatment Effectiveness	Costs
	regenerable resin			Plant		
		Lab Study		ORNL comparison study for bifunctional resins		
Rohm and Hass Corporation Amberlite PWA-2	Rohm and Hass developed non regenerable NSF 61 certified resin	Full Scale-Operational	2000 gpm	Aerojet, Sacramento,CA	50 ppb to <4 ppb	
Rohm and Hass Corporation Amberlite PWA-55	Commercially available resin	Full Scale-Operational	1000 gpm	W. San Martin Colony and County Wells	15 ppb to <4 ppb	
Oak Ridge National Laboratory (ORNL) and University of Tennessee (UT) Purolite A-530E Bifunctional resin	ORNL and UT developed bifunctional resin which had quaternary ammonium groups with large and small alkyl groups resulting in highly selective resin	Full Scale-Planned	25 gpm	Stringfellow site, Riverside CA.High TDS including sulfate and nitrates make the process tedious and frequent regeneration or changeouts with no brine disposal options	30 ppb to < 4 ppb	
BIOLOGICAL REDUCTION						
Envirogen/US Filter- Envirex fluidized bed reactors (FBR) with GAC media	Fluidized bed reactors with granular activated carbon media. Typically, ethanol is used as the electron acceptor					
		Full Scale-Operational	5300 gpm	Aerojet, Rancho Cordova	< 4 µg/L	
Applied research Associates, Inc.	Custom Designed Biological Treatment system	Full Scale-Operational		Thiokol, Brigham City, Utah. Full Scale continuously stirred tank reactor biological system operating since December 1997	> 5000 mg/L to 4-400 µg/L	\$0.35 to \$1.00/gallon
		Designed	825 gpm	Kerr- McGee, Henderson, Nevada.		
Foster Wheeler/ Arcadis Packed Bed Bioreactor	Packed Bed Bioreactor	Pilot Scale		NASA JPL, Pasadena, CA.	<1mg/L to non detect	

Table F1-1: Perchlorate Contamination Treatment Technologies (CA EPA, 2004) (Continued)

Technology & Vendor Name	Technology Description	Scale/Status	Throughput	Projects	Treatment Effectiveness	Costs
Pennsylvania State University anaerobic packed bed bioreactor	anaerobic acetate and nutrients-fed packed bed reactor with sand and plastic media; hydrogen reactors	Pilot Scale		Crafton-Redlands Plume, Redlands, CA.	70 µg/L reduced to < 4µg/L	
Eco Mat Hall Reactor	The patented Hall reactor provides an efficient circulation pattern and utilizes a floating porous media, Ecolink, which has a very high surface area to volume ratio.	Commercial	~2 gpm	DOD facility, Southern California.	350 µg/L to < 9 µg/L	\$0.50/1000 gallons
Hollow Fiber Membrane Biofilm Reactors	Bruce E. Rittmann of Northwestern University patented a hollow-fiber membrane biofilm reactor that utilizes hydrogen as an electron donor to biologically degrade perchlorate.	Pilot Scale	0.3 gpm	La Puente, CA.		
IN-SITU BIOLOGICAL TREATMENT						
GeoSyntec Consultants	Groundwater is extracted, then amended with acetate before being reinjected at an upgradient location. Optimally system is operated and monitored to ensure a closed groundwater recirculation loop.	Pilot Scale - Completed		Aerojet, Sacramento.	12mg/L reduced to < 4µg/L	

Table F1-1: Perchlorate Contamination Treatment Technologies (CA EPA, 2004) (Continued)

Technology & Vendor Name	Technology Description	Scale/Status	Throughput	Projects	Treatment Effectiveness	Costs
		Pilot Scale - Completed		AMPAC (formerly Pepcon) facility, Nevada. The electron donor was switeched from ethanol to citrate after 3 months due to fouling problems. Nitrates and chlorates are preferentially biodegraded before perchlorate.	After 160 days of operation 500 to 800 ppb reduced to 2 ppb	
Aerojet, Sacramento	Injection of amended water to remediate a perchlorate contaminated groundwater	Pilot Scale - Completed		Several tests have been done		
		Pilot Test - Planned		Horizontal well used to inject ammended water		
		Pilot Test - Planned		Ammended water addition to contaminated aquifer via a percolation pond.		
Groundwater Barrier Trench with cotton seed meal and cotton seed	Groundwater collection trench constructed with composting materials, cotton seed meal and cotton seed.	Full Scale - Operational		Naval Weapons Industrial Reserve Plant, McGregor, Texas.	27,000 µg/L reduced to < 4 µg/L	
NASA JPL Pasadena/Arcadis	Injection of corn syrup or other carbon source as the electron donor to promote biodegradation of perchlorate	Full Scale - Operational		NASA JPL Pasadena, CA.		
Solutions IES	Biologically active permeable barrier-injection of corn syrup or other carbon source as the electron donor to promote biodegradation of perchlorate	Full Scale - Proposed		Edwards AFB.		

Table F1-1: Perchlorate Contamination Treatment Technologies (CA EPA, 2004) (Continued)

Technology & Vendor Name	Technology Description	Scale/Status	Throughput	Projects	Treatment Effectiveness	Costs
Los Alamos National Laboratory	A multilayer permeable reactive barrier. The PRB incorporates a sequence of four reactive media layers to immobilize or destroy a suite of contaminants present in alluvial groundwater, including Sr-90, Pu-238, 239, 240, Am-241, perchlorate, and nitrate. The four sequential media cells consist of gravel sized scoria, apatite, pecan shells, and cottonseed with an admixture of gravel (biobarrier) and limestone.	Full Scale - Operational		LANL, Mortandad Canyon, NM.	Bench Scale results. Perchlorate reduced from 120 ppb to 35 ppb.	\$900,000 to install
GRANULAR ACTIVATED CARBON (GAC)						
Granular Activated Carbon	GAC system initially installed to treat VOC contamination for drinking water supply was later found effective to treat low concentrations of perchlorate	Full Scale - Operational		Crafton-Redlands Plume, City of Redlands, CA.	60 to 138 µg/L influent concentration . Effluent concentration not available right now.	

Table F1-1: Perchlorate Contamination Treatment Technologies (CA EPA, 2004) (Continued)

Technology & Vendor Name	Technology Description	Scale/Status	Throughput	Projects	Treatment Effectiveness	Costs
	A liquid phase GAC system	Full Scale - Operational	100 gpm	Edwards Site 113,	Influent perchlorate concentrations were 92 µg/L but the initial reports indicated that the system is ineffective in removing perchlorate.	
	Cocunut carbon to treat low levels	Full Scale Testing Planned		City of Monterey Park, Well 5		
COMPOSTING/ IN SITU TREATMENT (Contaminated Soil)						
GeoSyntec Consultants	Anaerobic composting of perchlorate-contaminated soils	Pilot Demonstration	20 yards	Aerojet, Sacramento, CA.	Maximum detected perchlorate concentration of 4200 mg/kg. Average 23 mg/Kg to about 0.1 mg/Kg in seven days.	
In situ biological treatment	In situ biological treatment of perchlorate contaminated soil using chicken manure, cow manure, and ethanol as suitable carbon sources.	Bench Scale-Completed Full Scale - Planned		Long Horn Army Ammunitions Plant, Texas.	Perchlorate reduced to below detection limit after 10 months.	estimated: \$25-50/yards

Table F1-1: Perchlorate Contamination Treatment Technologies (CA EPA, 2004) (Continued)

Technology & Vendor Name	Technology Description	Scale/Status	Throughput	Projects	Treatment Effectiveness	Costs
Soil Composting	Soil Composting	Full Scale		Pueblo Army Depot, Colorado.	Results unavailable	
Soil Bioremediation	Anaerobic composting of perchlorate soils	Full Scale and one planned	1500 cubic yards in full scale operations and 2400 yards planned	Boeing, Santa Susana Field Laboratory, Ventura Co.,CA is in full scale soil bioremediation process and Boeing, Sacramento is planning one.		
Anaerobic Soil Composting	Mixing in compost as nutrient to allow soil microbes to degrade perchlorate under anoxic condition	Planned		United Technologies Corp., located southeast of San Jose, CA.		
Anaerobic Soil Composting	Anaerobic composting	Feasibility Studies		Edwards Air Force Base.		
BIOLOGICALLY ACTIVE CARBON						
Biologically Active Carbon	Biologically active carbon filtration can effectively remove low levels of nitrate and perchlorate under anaerobic conditions with the addition of an electron donor.	Pilot Scale				
MEMBRANE FILTRATION						
Reverse Osmosis	Water is forced through a semi permeable membrane.	No applications		None		

Table F1-1: Perchlorate Contamination Treatment Technologies (CA EPA, 2004) (Continued)

Technology & Vendor Name	Technology Description	Scale/Status	Throughput	Projects	Treatment Effectiveness	Costs
Nanofiltration	A partially permeable membrane is used to preferentially separate different fluids or ions. Nanofiltration generally works for particle sizes over 10 angstroms. Perchlorate ion being 3.5 angstroms it might not prove to be a very useful technology for perchlorate removal	No applications		None		
Electrodialysis	Water is passed through channels of alternating semi permeable and permeable membranes, while being exposed to an electrical field	Pilot Scale-completed	7.4 gpm	Magna Water Co.,Utah.	Perchlorate removal rates stabilized in the low 70 percent range; higher removal rates (94%) could be achieved with a larger system	\$1.10 to \$1.50 / 1000 gallons
CHEMICAL REDUCTION						
UV Light/ Zero Valent Iron Reduction	Lab studies indicate that perchlorate can be reduced by iron (FeO) under anoxic conditions and the UV light can accelerate the reaction rate for practical application.	Laboratory Research		As of June 9, 2003, the San Diego office of Technology Transfer was seeking funds to commence six months of field testing to develop a commercial prototype		

Table F1-1: Perchlorate Contamination Treatment Technologies (CA EPA, 2004) (Continued)

Technology & Vendor Name	Technology Description	Scale/Status	Throughput	Projects	Treatment Effectiveness	Costs
Titanium +3 Chemical Reduction	Gorgetown University has developed a technique using titanous ions to chemically reduce perchlorate. Several new organic ligands have been developed that have shown to catalyze reduction of perchlorate by titanous ions to titanium oxide and chloride in acidic aqueous media.	Laboratory Research				
Electrochemical Reduction	A bench scale study of electrochemical reduction of perchlorate was conducted using two chambered batch reactor systems.	Laboratory Research				
ELECTROCHEMICAL						
Capacitative Deionization carbon aerogel	Influent water containing salts enters space between two carbon-aerogel electrodes; electrostatic field forces ions into aerogel, where they are held and purified water leaves the space between the electrodes.	Research and Development		CDT systems Inc. is planning to install this system at the municipal water treatment plant in Carlsbad, California.		

Table F1-1: Perchlorate Contamination Treatment Technologies (CA EPA, 2004) (Continued)

Technology & Vendor Name	Technology Description	Scale/Status	Throughput	Projects	Treatment Effectiveness	Costs
Capacitive Deionization Flow thorough Capacitor	The flow through Capcator is made up of alternating electrodes of porous activated carbon. With application of small voltage, dissolved salts in the water moving through the capacitor are attracted to the high surface are carbon and removed. Once the capacitor is fully charged the electrodes are shorted to regenerate the capcitor, causing adsorbed contaminants to be released as a small volume of concentrated liquids	Research and Development		The flow through capacitor technology is covered by a number of patents and Biosource Inc. indicated in May, 2004 that it will be used by the military to purify water and it shall be used in Iraq also.		
PHYTO REMEDIATION						
Willow trees	In bench scale tests willow trees successfully treated water contaminated with perchlorate. Rhizodegradation accounted for most of the removal of perchlorate with little uptake into the plant.	Bench Scale				

Table F1-1: Perchlorate Contamination Treatment Technologies (CA EPA, 2004) (Continued)

Technology & Vendor Name	Technology Description	Scale/Status	Throughput	Projects	Treatment Effectiveness	Costs
Salt Cedar Trees	stalks of the plant picked up significant concentrations of perchlorate per gram tissue	Research				
Contained Wetlands	Lawrence Livermore National Laboratory engineered plants to assimilate or degrade nitrate and perchlorate in water via the interaction of the contaminant with plant roots and their associated rhizosphere microorganisms.	Pilot Study-Completed		A containerized wetland system designed to remove nitrate and perchlorate from groundwater was tested over a seven-month period at Lawrence Livermore National Laboratory	Removal of perchlorate below 4 µg/L	